Supporting Information

Brønsted acid cocatalysis in visible-light photocatalytic intramolecular coupling of tertiary amines: efficient synthesis of indoles under mild conditions

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A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H-NMR) spectra and carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz and 100 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane or referenced to residual solvent. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane or referenced to residual solvent. Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). High resolution mass spectrometry (ESI) were carried out using a Waters Quatro Macro triple quadrupole mass spectrometer Mass spectra (EI) were measured on a Waters Micromass GCT spectrometer. Melting points were measured on a XT3A apparatus.

Starting Materials. All reactions were performed under nitrogen atmosphere in Schlenk-tube unless otherwise noted. Distilled water was sparged with nitrogen and used in the photoredox reactions. All other solvents, including those for NMR analysis, were used without further purification. All chemicals were purchased from commercial sources and used as received.

B: Supplementary Figures

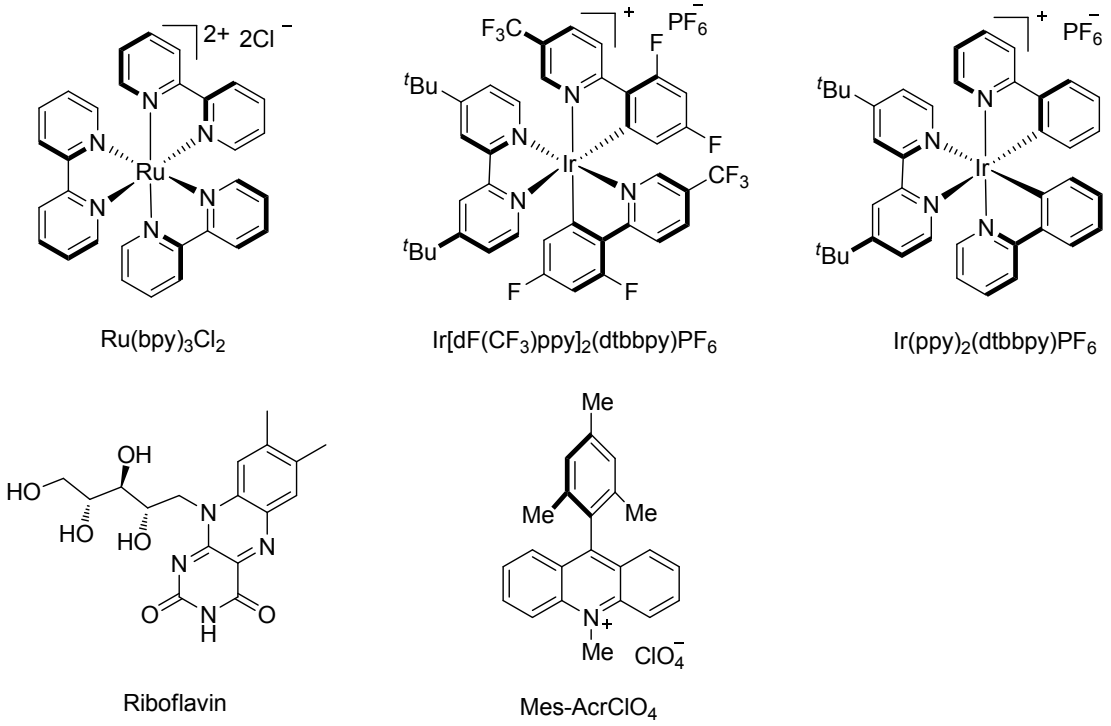
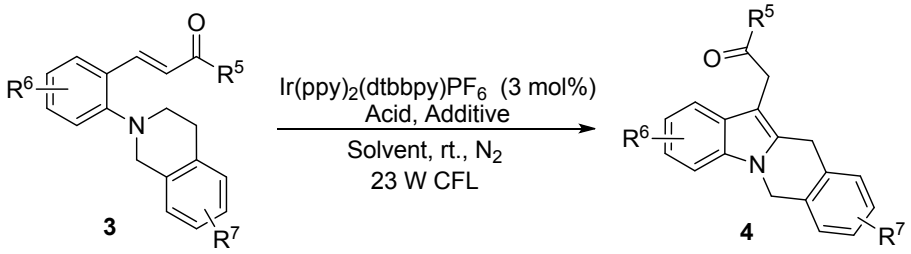


Figure S1. Photocatalyst screened for synthesis of indole derivatives.



entry	Acid	Additive	Solvent	yield (%)[b]
1	TFA (20 mol%)	None	CH_3CN	38
2	TFA (30 mol%)	None	CH_3CN	42
3	TFA (40 mol%)	None	CH_3CN	36
4	$(PhO)_2PO_2H$ (30 mol%)	None	CH_3CN	34
5	TFA (30 mol%)	None	DMF	31
6	TFA (30 mol%)	None	DMSO	41
7	TFA (30 mol%)	None	DCM	49
8	TFA (30 mol%)	None	DCE	50
9	TFA (30 mol%)	TBHP (1 eq.)	DMF	25

10	TFA (30 mol%)	DDQ (1 eq.)	DMF	12
11	TFA (30 mol%)	Chalcone (1 eq.)	DMF	79
12	None	Chalcone (1 eq.)	DMF	NR
13[c]	TFA (30 mol%)	Chalcone (1 eq.)	DMF	NR

[a] All reactions were performed on a 0.3 mmol scale using a 3 mol% photocatalyst, 1.5 mL solvent, and a 23 W CFL as the light source, at room temperature, 12 h. [b] Yield of the isolated product. [c] In the absence of light source. TFA = trifluoroacetic acid; $(PhO)_2PO_2H$ = diphenylphosphoric acid.

Figure S2. Exploratory studies on synthesis of indole derivatives.

C: Synthesis and Characterizations of Substrates

Method:

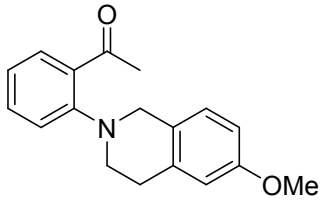
1a-r were prepared following the literature procedures.[1] **3a-l** were prepared following the literature procedures.[2]

References

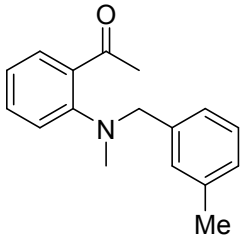
[1] W.-t. Wei, X.-j. Dong, S.-z. Nie, Y.-y. Chen, X.-j. Zhang, M. Yan, *Org. Lett.* 2013, **15**, 6018.

[2] P. Kohls, D. Jadhav, G. Pandey, O. Reiser, *Org. Lett.* 2012, **14**, 672.

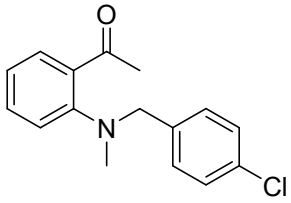
Characterization of new substrates



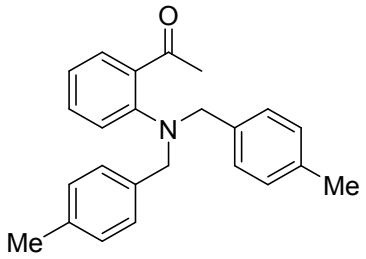
1-(2-(6-methoxy-3,4-dihydroisoquinolin-2(1H)-yl)phenyl)ethan-1-one (1c). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.36 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.09-7.02 (m, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.75 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.69 (d, *J* = 2.6 Hz, 1H), 4.14 (s, 2H), 3.79 (s, 3H), 3.33 (t, *J* = 5.8 Hz, 2H), 2.96 (t, *J* = 5.9 Hz, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.5, 158.2, 151.1, 135.3, 135.1, 132.0, 129.4, 127.3, 126.5, 122.3, 118.9, 113.4, 112.4, 55.3, 54.6, 51.2, 29.3, 29.2; HRMS (ESI) calculated for $C_{18}H_{20}NO_2$ $(M+H)^+$ 282.1489, found 282.1492.



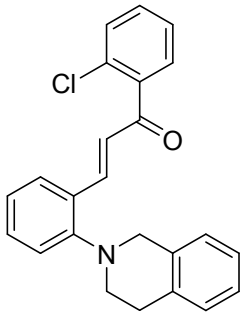
1-(2-(methyl(3-methylbenzyl)amino)phenyl)ethan-1-one (1m). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.35 (ddd, *J* = 8.5, 7.3, 1.7 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.04-6.93 (m, 4H), 4.18 (s, 2H), 2.66 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.9, 151.4, 138.0, 137.3, 133.9, 131.8, 129.4, 129.2, 128.3, 128.1, 125.5, 121.1, 119.1, 60.7, 41.9, 29.4, 21.5; HRMS (ESI) calculated for $C_{17}H_{20}NO$ $(M+H)^+$ 254.1540, found 254.1544.



1-(2-((4-chlorobenzyl)(methyl)amino)phenyl)ethan-1-one (1n). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.33 (td, *J* = 8.3, 7.9, 1.6 Hz, 1H), 7.24 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.02-6.93 (m, 2H), 4.15 (s, 2H), 2.64 (dd, *J* = 3.3, 1.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.6, 150.9, 135.9, 134.0, 133.1, 131.8, 129.8, 129.4, 128.6, 121.5, 119.3, 60.1, 41.8, 29.5; HRMS (ESI) calculated for $C_{16}H_{17}ClNO$ $(M+H)^+$ 274.0994, found 274.0996.

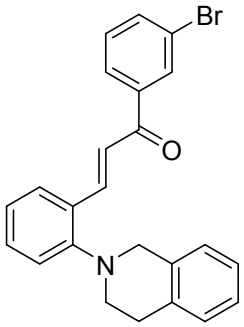


1-(2-(bis(4-methylbenzyl)amino)phenyl)ethan-1-one (1q). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.24 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 4H), 7.01-6.93 (m, 5H), 6.87 (dd, *J* = 8.2, 1.0 Hz, 1H), 4.06 (s, 4H), 2.71 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.9, 150.1, 137.0, 135.3, 134.0, 131.5, 129.6, 129.1, 129.0, 121.9, 121.5, 56.9, 29.7, 21.3; HRMS (ESI) calculated for $C_{24}H_{26}NO$ $(M+H)^+$ 344.2009, found 344.2012.

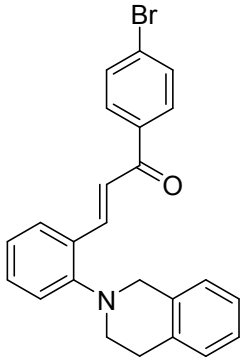


(E)-1-(2-chlorophenyl)-3-(2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)prop-2-en-1-one (3b). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 16.3 Hz, 1H), 7.59-7.52 (m, 1H), 7.33-7.26 (m, 1H), 7.26-7.20 (m, 2H), 7.17 (td, *J* = 8.7, 8.1, 2.0 Hz, 1H), 7.11-7.04 (m, 3H), 7.01 (d, *J* = 7.9 Hz, 3H), 6.99-6.93 (m, 2H), 4.03 (s, 2H), 3.11 (t, *J* = 5.8 Hz, 2H), 2.68 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

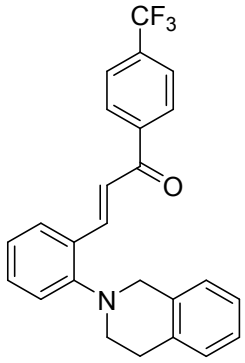
152.8, 145.2, 139.1, 134.4, 134.3, 131.7, 131.0, 130.9, 130.0, 128.9, 128.8, 128.4, 128.2, 126.7, 126.6, 126.4, 125.9, 123.0, 119.2, 54.4, 52.1, 29.4; HRMS (ESI) calculated for $C_{24}H_{21}ClNO$ $(M+H)^+$ 374.1307, found 374.1311.



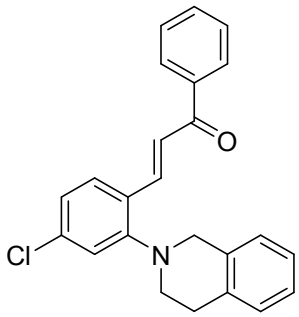
(E)-1-(3-bromophenyl)-3-(2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)prop-2-en-1-one (3c). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 15.8 Hz, 1H), 8.10 (d, *J* = 1.7 Hz, 1H), 7.79 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.67 (ddd, *J* = 16.3, 7.8, 1.7 Hz, 2H), 7.50 (d, *J* = 15.8 Hz, 1H), 7.40 (td, *J* = 7.7, 1.5 Hz, 1H), 7.29-7.21 (m, 1H), 7.22-7.13 (m, 4H), 7.16-7.05 (m, 2H), 4.24 (s, 2H), 3.32 (t, *J* = 5.8 Hz, 2H), 3.04 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.7, 153.1, 143.7, 140.2, 135.3, 134.5, 131.5, 130.1, 129.1, 128.9, 128.8, 127.0, 126.5, 126.3, 126.0, 122.9, 121.5, 119.4, 54.2, 52.2, 29.3; HRMS (ESI) calculated for $C_{24}H_{21}BrNO$ $(M+H)^+$ 418.0802, found 418.0805.



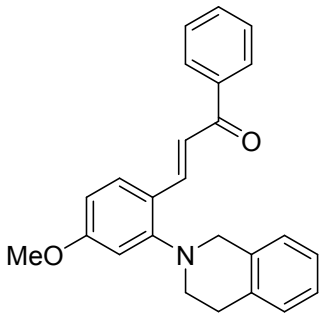
(E)-1-(4-bromophenyl)-3-(2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)prop-2-en-1-one (3d). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 15.8 Hz, 1H), 7.79-7.71 (m, 2H), 7.67 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.58-7.46 (m, 3H), 7.44-7.36 (m, 1H), 7.24-7.07 (m, 6H), 4.23 (s, 2H), 3.32 (t, *J* = 5.8 Hz, 2H), 3.04 (t, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 190.1, 153.0, 143.4, 137.1, 134.6, 134.5, 131.8, 131.4, 130.0, 129.2, 129.1, 128.9, 127.5, 126.5, 126.4, 126.0, 123.0, 121.7, 119.5, 54.4, 51.9, 29.4; HRMS (ESI) calculated for $C_{24}H_{21}BrNO$ $(M+H)^+$ 418.0802, found 418.0804.



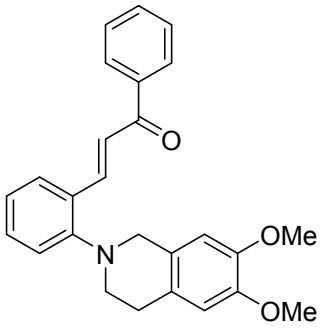
(E)-3-(2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3e). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 15.9 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 15.9 Hz, 1H), 7.41 (td, *J* = 7.7, 1.6 Hz, 1H), 7.25-7.03 (m, 6H), 4.22 (s, 2H), 3.32 (t, *J* = 5.8 Hz, 2H), 3.02 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 153.1, 144.2, 134.5, 131.6, 129.1, 128.8, 128.7, 126.6, 126.3, 126.0, 125.6, 125.5 (d, *J* = 3.8 Hz), 123.1, 122.0, 119.6, 54.6, 51.8, 29.4; HRMS (ESI) calculated for $C_{25}H_{21}F_3NO$ $(M+H)^+$ 408.1570, found 408.1573.



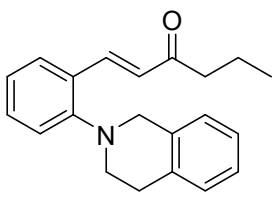
(E)-3-(4-chloro-2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)-1-phenylprop-2-en-1-one (3f). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 15.8 Hz, 1H), 7.95-7.88 (m, 2H), 7.63-7.51 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.24-7.16 (m, 2H), 7.09 (ddd, *J* = 14.9, 8.4, 2.0 Hz, 3H), 4.23 (s, 2H), 3.31 (t, *J* = 5.8 Hz, 2H), 3.05 (t, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 153.8, 141.6, 138.2, 136.7, 134.3, 134.0, 132.7, 129.8, 129.1, 128.6, 128.5, 127.4, 126.6, 126.4, 126.1, 122.9, 122.3, 119.6, 53.9, 52.0, 29.4; HRMS (ESI) calculated for $C_{24}H_{21}ClNO$ $(M+H)^+$ 374.1307, found 374.1310.



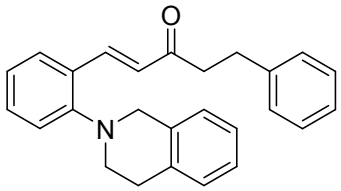
(E)-3-(2-(3,4-dihydroisoquinolin-2(1H)-yl)-4-methoxyphenyl)-1-phenylprop-2-en-1-one (3g). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 15.8 Hz, 1H), 7.93-7.82 (m, 2H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.54-7.46 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.18 (tdd, *J* = 8.8, 6.3, 2.0 Hz, 3H), 7.12-7.05 (m, 1H), 6.73-6.60 (m, 2H), 4.21 (s, 2H), 3.84 (s, 3H), 3.32 (t, *J* = 5.8 Hz, 2H), 3.04 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 162.4, 154.8 , 142.7, 138.6, 134.5, 132.3, 130.7, 129.1, 128.5, 128.4, 126.5, 126.4, 125.9, 121.8, 120.0, 107.9, 105.7, 55.4, 54.2, 52.0, 29.4; HRMS (ESI) calculated for $C_{25}H_{24}NO_2$ $(M+H)^+$ 370.1802, found 370.1805.



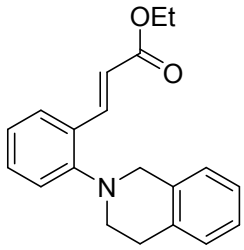
(E)-3-(2-(6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)phenyl)-1-phenylprop-2-en-1-one (3h). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 15.9 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.69 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.60 (d, *J* = 15.9 Hz, 1H), 7.57-7.50 (m, 1H), 7.47-7.35 (m, 3H), 7.17-7.07 (m, 2H), 6.68 (s, 1H), 6.59 (s, 1H), 4.18 (s, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 3.31 (t, *J* = 5.8 Hz, 2H), 2.95 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 152.9, 147.7, 147.4, 142.9, 138.3, 132.6, 131.1, 129.0, 128.5, 126.5, 126.4, 122.8, 122.1, 119.4, 111.7, 109.2, 56.0, 53.7, 52.0, 28.8; HRMS (ESI) calculated for $C_{26}H_{26}NO_3$ $(M+H)^+$ 400.1908, found 400.1913.



(E)-1-(2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)hex-1-en-3-one (3j). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 16.4 Hz, 1H), 7.55 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.37-7.29 (m, 1H), 7.18-7.14 (m, 3H), 7.12-7.01 (m, 3H), 6.68 (dd, *J* = 16.6, 1.3 Hz, 1H), 4.17 (s, 2H), 3.23 (t, *J* = 5.8 Hz, 2H), 3.01 (t, *J* = 5.9 Hz, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 1.66 (hd, *J* = 7.3, 1.3 Hz, 2H), 0.91 (td, *J* = 7.4, 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 152.5, 140.2, 134.3, 131.0, 129.1, 128.9, 128.1, 126.8, 126.5, 126.4, 126.0, 123.0, 119.2, 54.2, 52.2, 42.0, 29.5, 18.1, 14.0; HRMS (ESI) calculated for $C_{21}H_{24}NO$ $(M+H)^+$ 306.1853, found 306.1857.



(E)-1-(2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)-5-phenylpent-1-en-3-one (3k). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 16.5 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.42-7.35 (m, 1H), 7.27-7.23 (m, 1H), 7.21-7.11 (m, 8H), 7.11-7.05 (m, 2H), 6.71 (d, *J* = 16.5 Hz, 1H), 4.22 (s, 2H), 3.27 (t, *J* = 5.8 Hz, 2H), 3.01 (t, *J* = 5.9 Hz, 2H), 2.97 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 152.5, 141.2, 140.6, 134.5, 134.3, 131.1, 129.1, 128.8, 128.5, 128.4, 128.0, 126.5, 126.3, 126.0 (d, *J* = 3.7 Hz), 123.0, 119.2, 54.2, 52.1, 41.7, 30.4, 29.3; HRMS (ESI) calculated for $C_{26}H_{26}NO$ $(M+H)^+$ 368.2009, found 368.2012.



ethyl (E)-3-(2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)acrylate (3l). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 16.1 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.32-7.24 (m, 1H), 7.16-7.08 (m, 3H), 7.07-6.95 (m, 3H), 6.34 (d, *J* = 16.1 Hz, 1H), 4.17 (d, *J* = 7.5 Hz, 4H), 3.18 (t, *J* = 5.8 Hz, 2H), 2.97 (t, *J* = 5.8 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 152.2, 142.3, 134.7, 134.6, 130.8, 129.0, 128.7, 128.0, 126.4, 126.4, 125.9, 122.8, 119.0, 117.9, 60.4, 53.6, 52.5, 29.3, 14.4; HRMS (ESI) calculated for $C_{20}H_{22}NO_2$ $(M+H)^+$ 308.1646, found 308.1651.

D: Synthesis and Characterizations of Products.

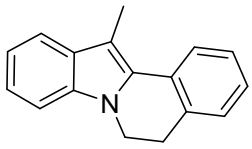
Method A:

Ketones (**1**, 0.3 mmol, 1.0 equiv), diphenylphosphoric acid (30.0 mg, 0.12 mmol, 40 mol%) and $Ir(ppy)_2(dtbbpy)PF_6$ (7.5 mg, 0.009 mmol, 3 mol%) were placed in a Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen. DMF degassed with N_2 was then added. The reaction mixture was irradiated with a 23 W CFL (at approximately 2 cm away from the light source) at room temperature (using a fan to maintain the temperature at about 25 ˚C). Upon completion of the reaction, the resulting mixture was extracted with dichloromethane (20 mL × 3). The combined organics were died over anhydrous Na_2SO_4, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum/ethyl acetate as the eluent to give the corresponding product.

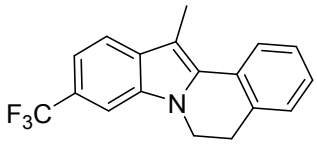
Method B:

Ketenes (**3**, 0.3 mmol, 1.0 equiv), trifluoroacetic acid (10.3 mg, 0.09 mmol, 30 mol%), chalcone (62.5 mg, 0.3 mmol, 1.0 equiv) and $Ir(ppy)_2(dtbbpy)PF_6$ (7.5 mg, 0.009 mmol, 3 mol%) were placed in a Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen. DCE degassed with N_2 was then added. The reaction mixture was irradiated with a 23 W CFL (at approximately 2 cm away from the light source) at room temperature (using a fan to maintain the temperature at about 25 ˚C). Upon completion of the reaction, the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum/ethyl acetate as the eluent to give the corresponding product.

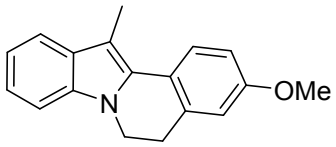
Characterization of Fluorinated Products:



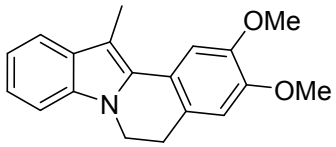
12-methyl-5,6-dihydroindolo[2,1-a]isoquinoline (2a). White solid, mp 148.1-151.8 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.26 (t, *J* = 6.9 Hz, 2H), 7.19 (ddd, *J* = 9.8, 6.0, 2.5 Hz, 2H), 7.14-7.06 (m, 1H), 4.16 (t, *J* = 6.3 Hz, 2H), 3.08 (t, *J* = 6.3 Hz, 2H), 2.62 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 133.5, 130.7, 130.4, 129.4, 128.4, 127.1, 126.6, 125.6, 122.0, 119.1, 118.9, 108.6, 107.2, 40.1, 30.3, 10.8; HRMS (ESI) calculated for $C_{17}H_{16}N$ $(M+H)^+$ 234.1278, found 234.1282.



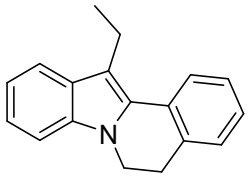
12-methyl-9-(trifluoromethyl)-5,6-dihydroindolo[2,1-a]isoquinoline (2b). White solid, mp 126.6-128.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.45 (s, 1H), 7.28-7.19 (m, 2H), 7.14 (dd, *J* = 8.8, 1.9 Hz, 2H), 4.08 (t, *J* = 6.3 Hz, 2H), 2.99 (t, *J* = 6.3 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.2, 133.7, 133.3, 131.6, 129.6, 128.5, 127.4, 127.3, 125.9, 125.4 (q, *J* = 269 Hz), 123.7 (q, *J* = 32 Hz), 119.1, 115.6 (q, *J* = 4 Hz), 107.4, 106.1 (q, *J* = 5 Hz), 40.3, 30.0, 10.7; HRMS (ESI) calculated for $C_{18}H_{13}NF_3$ $(M-H)^-$ 300.1006, found 300.1009.



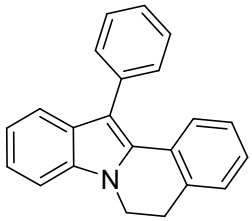
3-methoxy-12-methyl-5,6-dihydroindolo[2,1-a]isoquinoline (2c). White solid, mp 122.5-123.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.6 Hz, 1H), 7.58 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.26 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.18 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.12-7.06 (m, 1H), 6.90 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.83 (d, *J* = 2.7 Hz, 1H), 4.18 (t, *J* = 6.3 Hz, 2H), 3.84 (s, 3H), 3.08 (t, *J* = 6.3 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 135.2, 135.1, 130.9, 129.5, 126.9, 123.3, 121.4, 118.9, 118.5, 114.0, 112.5, 108.4, 105.5, 55.4, 40.0, 30.6, 10.7; HRMS (ESI) calculated for $C_{18}H_{18}NO$ $(M+H)^+$ 264.1383, found 264.1385.



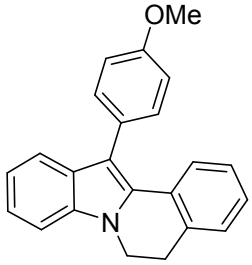
2,3-dimethoxy-12-methyl-5,6-dihydroindolo[2,1-a]isoquinoline (2d). White solid, mp 125.0-127.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.39 (s, 1H), 7.24 (d, *J* = 10.9 Hz, 1H), 7.22-7.15 (m, 1H), 7.13-7.02 (m, 1H), 6.79 (s, 1H), 4.17 (t, *J* = 6.3 Hz, 2H), 3.96 (s, 3H), 3.92 (s, 3H), 3.05 (t, *J* = 6.3 Hz, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ148.0, 147.9, 135.2, 130.9, 129.5, 126.3, 123.0, 121.5, 118.9, 118.5, 111.7, 109.2, 108.4, 105.4, 56.1, 56.0, 40.2, 29.8, 10.6; HRMS (ESI) calculated for $C_{19}H_{20}NO_2$ $(M+H)^+$ 294.1490, found 294.1493.



12-ethyl-5,6-dihydroindolo[2,1-a]isoquinoline (2e). White solid, mp 134.5-135.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.67 (m, 1H), 7.54 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.24 (td, *J* = 7.5, 1.6 Hz, 1H), 7.21-7.04 (m, 4H), 7.01 (tt, *J* = 8.1, 1.3 Hz, 1H), 4.07 (t, *J* = 6.3 Hz, 2H), 3.16-2.87 (m, 4H), 1.30 (td, *J* = 7.5, 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.5, 133.7, 130.2, 130.1, 128.6, 128.5, 127.3, 126.8, 125.4, 122.0, 119.1, 118.9, 114.3, 108.8, 40.1, 30.3, 18.5, 15.3; HRMS (ESI) calculated for $C_{18}H_{18}N$ $(M+H)^+$ 248.1434, found 248.1439.

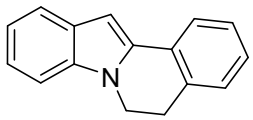


12-phenyl-5,6-dihydroindolo[2,1-a]isoquinoline (2f). White solid, mp 156.3-159.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.6 Hz, 3H), 7.42-7.35 (m, 2H), 7.30 (dd, *J* = 10.4, 6.5 Hz, 3H), 7.20-7.13 (m, 2H), 7.10-6.99 (m, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 4.19 (t, *J* = 6.3 Hz, 2H), 3.13 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.8, 135.5, 133.5, 130.5, 129.2, 128.8, 128.2, 127.2, 126.7, 126.7, 126.1, 122.3, 120.0, 119.6, 113.9, 108.8, 40.3, 29.9; HRMS (ESI) calculated for $C_{22}H_{18}N$ $(M+H)^+$ 296.1434, found 296.1436.

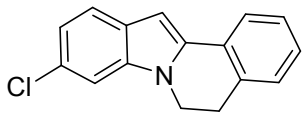


12-(4-methoxyphenyl)-5,6-dihydroindolo[2,1-a]isoquinoline (2g). White solid, mp 208.5-209.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.40-7.28 (m, 3H), 7.28-7.21 (m, 1H), 7.17-7.10 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 5H), 4.15 (t, *J* = 6.3 Hz, 2H), 3.79 (s, 3H), 3.08 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 135.5, 133.5, 131.5, 130.4, 129.4, 129.0, 128.3, 128.0, 127.1, 126.7, 126.0,

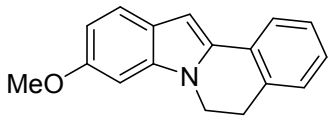
122.3, 119.9, 119.6, 114.3, 113.6, 108.8, 55.3, 40.3, 29.9; HRMS (ESI) calculated for $C_{23}H_{20}NO$ $(M+H)^+$ 326.1539, found 326.1544.



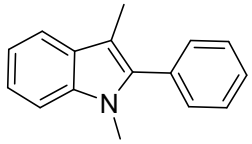
5,6-dihydroindolo[2,1-a]isoquinoline (2h). White solid, mp 127-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.63 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.37-7.28 (m, 2H), 7.26-7.16 (m, 3H), 7.10 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.87 (d, *J* = 0.8 Hz, 1H), 4.25 (t, *J* = 6.5 Hz, 2H), 3.19 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 135.6, 132.2, 129.0, 128.8, 128.3, 127.4, 127.2, 124.4, 121.7, 120.7, 119.9, 108.9, 96.4, 40.1, 29.2; HRMS (ESI) calculated for $C_{16}H_{14}N$ $(M+H)^+$ 220.1121, found 220.1125.



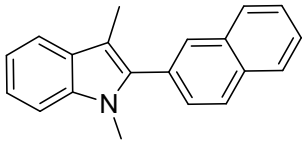
9-chloro-5,6-dihydroindolo[2,1-a]isoquinoline (2i). White solid, mp 145.2-146.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.62 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.254-7.13 (m, 4H), 6.98 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.74 (d, *J* = 0.9 Hz, 1H), 4.12 (t, *J* = 6.5 Hz, 2H), 3.10 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 136.4, 132.0, 128.6, 128.4, 127.6 (d, *J* = 19.8 Hz), 127.3 (d, *J* = 4.3 Hz), 124.4, 121.5, 120.5, 109.1, 96.5, 40.2, 29.0; HRMS (ESI) calculated for $C_{16}H_{13}ClN$ $(M+H)^+$ 254.0732, found 254.0735.



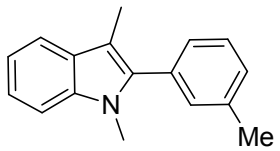
9-methoxy-5,6-dihydroindolo[2,1-a]isoquinoline (2j). White solid, mp 157-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.29 (td, *J* = 7.5, 1.5 Hz, 1H), 7.24-7.15 (m, 2H), 6.81-6.71 (m, 3H), 4.20 (t, *J* = 6.5 Hz, 2H), 3.89 (s, 3H), 3.18 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 137.4, 134.8, 131.6, 129.2, 128.2, 127.2, 126.9, 123.9, 123.1, 121.4, 109.8, 96.4, 92.6, 55.7, 40.1, 29.2; HRMS (ESI) calculated for $C_{17}H_{16}NO$ $(M+H)^+$ 250.1227, found 250.1229.



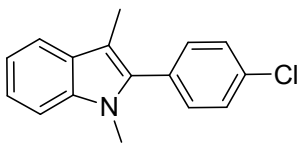
1,3-dimethyl-2-phenyl-1H-indole (2k). White solid, mp 65.1-66.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.48 (ddd, *J* = 7.8, 6.1, 1.2 Hz, 2H), 7.40 (td, *J* = 6.8, 1.8 Hz, 3H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.25 (s, 1H), 7.20-7.11 (m, 1H), 3.61 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 137.3, 132.2, 130.7, 128.5, 128.3, 127.7, 121.7, 119.1, 118.8, 109.2, 108.6, 30.9, 9.4; HRMS (ESI) calculated for $C_{16}H_{16}N$ $(M+H)^+$ 222.1272, found 222.1276.



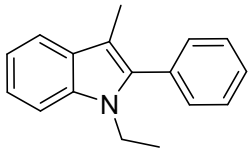
1,3-dimethyl-2-(naphthalen-2-yl)-1H-indole (2l). White solid, mp 206.3-207.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (t, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.55-7.40 (m, 4H), 7.33 (dd, *J* = 18.5, 7.8 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.18 (s, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 3.35 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 135.9, 133.6, 133.2, 129.9, 129.5, 128.9, 128.4, 128.3, 126.6, 126.2, 126.1, 125.3, 121.6, 119.0, 118.8, 109.9, 109.2, 30.6, 9.3; HRMS (ESI) calculated for $C_{20}H_{18}N$ $(M+H)^+$ 272.1434, found 272.1439.



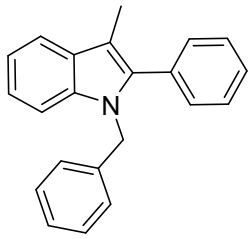
1,3-dimethyl-2-(m-tolyl)-1H-indole (2m). White solid, mp 132.5-134.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.26-7.12 (m, 5H), 3.60 (s, 3H), 2.43 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.8, 137.2, 132.1, 131.3, 128.6, 128.5, 128.2, 127.8, 121.7, 119.1, 118.8, 109.2, 108.4, 31.0, 21.6, 9.4; HRMS (ESI) calculated for $C_{17}H_{18}N$ $(M+H)^+$ 236.1434, found 226.1438.



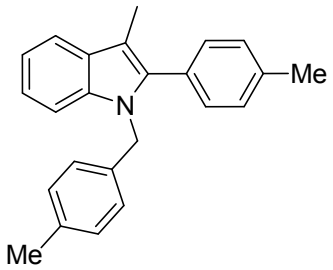
2-(4-chlorophenyl)-1,3-dimethyl-1H-indole (2n). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 3H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 3.58 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 136.4, 133.9, 131.9, 130.7, 128.7, 128.4, 122.1, 119.3, 119.0, 109.3, 109.1, 31.0, 9.4; HRMS (ESI) calculated for $C_{16}H_{15}ClN$ $(M+H)^+$ 256.0888, found 256.0891.



1-ethyl-3-methyl-2-phenyl-1H-indole (2o). White solid, mp 61.4-62.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.51-7.43 (m, 2H), 7.43-7.32 (m, 4H), 7.28-7.19 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 2.24 (d, *J* = 1.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 136.0, 132.5, 130.6, 128.7, 128.4, 127.8, 121.6, 119.0, 118.9, 109.5, 108.8, 38.6, 15.3, 9.2; HRMS (ESI) calculated for $C_{17}H_{18}NO$ $(M+H)^+$ 236.1434, found 236.1438.

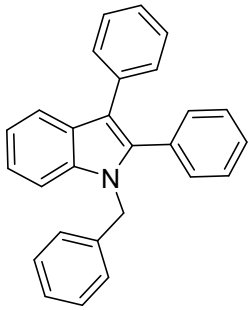


1-benzyl-3-methyl-2-phenyl-1H-indole (2p). White solid, mp 126.6-127.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (ddd, *J* = 6.9, 3.2, 1.5 Hz, 1H), 7.34-7.19 (m, 5H), 7.08 (dtt, *J* = 9.5, 6.5, 2.7 Hz, 6H), 6.85 (dd, *J* = 7.4, 2.0 Hz, 2H), 5.13 (s, 2H), 2.22 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 137.8, 136.9, 132.1, 130.6, 128.9, 128.6, 128.4, 127.9, 127.1, 126.1, 122.0, 119.5, 118.9, 110.2, 109.2, 47.6, 9.5; HRMS (ESI) calculated for $C_{22}H_{20}N$ $(M+H)^+$ 298.1590, found 298.1595.

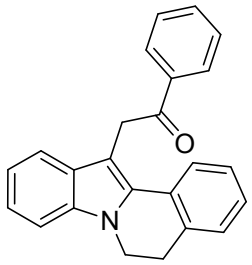


3-methyl-1-(4-methylbenzyl)-2-(p-tolyl)-1H-indole (2q). White solid, mp 145.6-

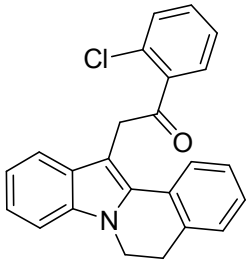
146.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.57 (m, 1H), 7.25-7.17 (m, 4H), 7.13 (dd, *J* = 5.9, 3.7 Hz, 3H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 7.9 Hz, 2H), 5.18 (s, 2H), 2.38 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 137.7, 136.8, 136.5, 135.6, 130.5, 129.3, 129.1, 129.1, 128.9, 126.0, 121.8, 119.3, 118.8, 110.3, 108.8, 47.4, 21.4, 21.1, 9.5; HRMS (ESI) calculated for $C_{24}H_{24}N$ $(M+H)^+$ 326.1904, found 326.1908.



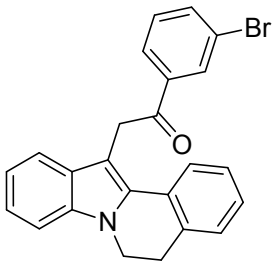
1-benzyl-2,3-diphenyl-1H-indole (2r). White solid, mp 139-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.68 (m, 1H), 7.31-7.07 (m, 16H), 6.99-6.88 (m, 2H), 5.21 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 136.8, 135.9, 134.1, 130.7, 130.0, 128.9, 127.6, 127.3, 127.1, 126.3, 126.1, 125.1, 124.5, 121.3, 119.4, 118.7, 114.6, 109.5, 46.6; HRMS (ESI) calculated for $C_{27}H_{22}N$ $(M+H)^+$ 360.1747, found 360.1752.



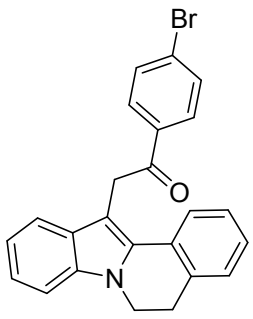
2-(5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)-1-phenylethanone (4a). White solid, mp 198.9-200.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 6.9 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 3H), 7.29 (dd, *J* = 14.4, 7.9 Hz, 2H), 7.24-7.16 (m, 3H), 7.07 (t, *J* = 7.4 Hz, 1H), 4.75 (s, 2H), 4.23 (t, *J* = 6.3 Hz, 2H), 3.10 (t, *J* = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 137.0, 135.6, 134.0, 133.2, 132.5, 129.5, 129.1, 128.7, 128.5, 127.3, 127.2, 125.3, 122.2, 119.6, 118.8, 108.9, 104.1, 40.2, 36.1, 30.2; HRMS (ESI) calculated for $C_{24}H_{20}NO$ $(M+H)^+$ 338.1540, found 338.1545.



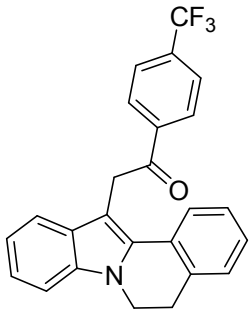
1-(2-chlorophenyl)-2-(5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)ethanone (4b). White solid, mp 195.3-196.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.35-7.28 (m, 4H), 7.26-7.17 (m, 4H), 7.06 (t, *J* = 7.5 Hz, 1H), 4.70 (s, 2H), 4.23 (t, *J* = 6.3 Hz, 2H), 3.08 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 140.0, 135.5, 133.9, 132.8, 131.3, 130.4, 130.2, 129.3, 128.9, 128.7, 128.4, 127.4, 127.4, 126.8, 125.5, 122.2, 119.6, 118.8, 108.8, 103.2, 40.4, 40.1, 30.1; HRMS (ESI) calculated for $C_{24}H_{19}ClNO$ $(M+H)^+$ 372.1151, found 372.1154.



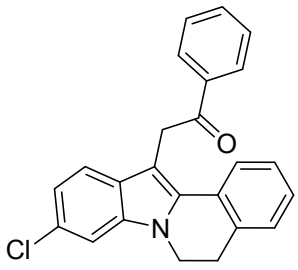
1-(3-bromophenyl)-2-(5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)ethanone (4c). White solid, mp 201.3-203.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.1 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.35-7.29 (m, 3H), 7.27-7.19 (m, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 4.72 (s, 2H), 4.24 (t, *J* = 6.3 Hz, 2H), 3.11 (t, *J* = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 138.5, 136.0, 135.5, 134.1, 132.5, 131.6, 130.2, 129.4, 128.9, 128.5, 127.4, 126.9, 125.1, 123.0, 122.3, 119.7, 118.7, 109.0, 103.5, 40.2, 36.4, 30.2; HRMS (ESI) calculated for $C_{24}H_{19}BrNO$ $(M+H)^+$ 416.0645, found 416.0647.



1-(4-bromophenyl)-2-(5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)ethanone (4d). White solid, mp 198.7-200.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.62-7.56 (m, 3H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 8.8 Hz, 3H), 7.25-7.19 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.72 (s, 2H), 4.26 (t, *J* = 6.3 Hz, 2H), 3.13 (t, *J* = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 135.6, 135.5, 134.0, 132.4, 131.9, 130.0, 129.4, 128.9, 128.5, 128.3, 127.4, 125.2, 122.3, 119.7, 118.7, 109.0, 103.7, 40.1, 36.3, 30.2; HRMS (ESI) calculated for $C_{24}H_{19}BrNO$ $(M+H)^+$ 416.0645, found 416.0659.

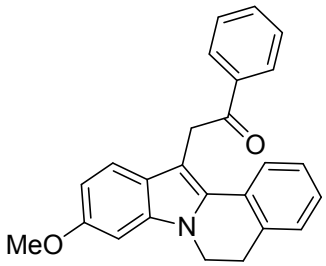


2-(5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)-1-(4-(trifluoromethyl)phenyl)ethanone (4e). White solid, mp 209-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 9.1 Hz, 2H), 7.28-7.19 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 4.76 (s, 2H), 4.25 (t, *J* = 6.2 Hz, 2H), 3.11 (t, *J* = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 139.5, 135.5, 134.5, 134.2, 134.1, 132.5, 129.3, 128.8, 128.8, 128.6, 127.4 (d, *J* = 7.8 Hz), 125.7 (d, *J* = 3.7 Hz), 125.1, 125.0, 122.3 (d, *J* = 6.9 Hz), 119.8, 118.6, 109.0, 103.3, 40.2, 36.7, 30.2; HRMS (ESI) calculated for $C_{25}H_{19}F_3NO$ $(M+H)^+$ 406.1414, found 406.1418.

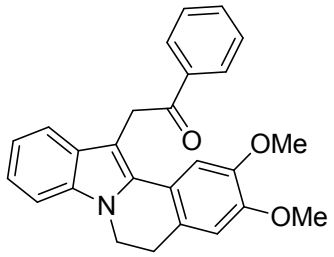


2-(9-chloro-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)-1-phenylethanone (4f). White solid, mp 184.1-185.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.52 (dt, *J* = 15.3, 5.5 Hz, 3H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.33-7.27 (m, 2H), 7.26-7.21 (m, 2H), 7.03 (d, *J* = 8.5 Hz, 1H), 4.73 (s, 2H), 4.20 (t, *J*

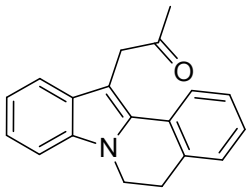
= 6.3 Hz, 2H), 3.12 (t, *J* = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 136.8, 135.9, 133.8, 133.3, 133.2, 129.1, 128.8, 128.5, 128.4, 128.1, 127.6, 127.5, 127.4, 125.2, 120.2, 119.7, 109.0, 104.2, 40.3, 36.0, 30.1; HRMS (ESI) calculated for $C_{24}H_{19}ClNO$ $(M+H)^+$ 372.1151, found 372.1154.



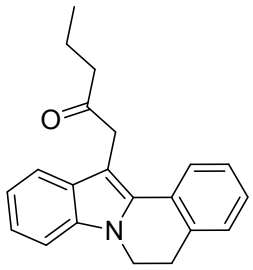
2-(9-methoxy-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)-1-phenylethanone (4g). White solid, mp 190.2-192.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.9 Hz, 2H), 7.63-7.52 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.20 (dd, *J* = 16.4, 8.7 Hz, 2H), 6.80-6.69 (m, 2H), 4.73 (s, 2H), 4.20 (t, *J* = 6.1 Hz, 2H), 3.87 (s, 3H), 3.11 (t, *J* = 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 156.8, 136.9, 136.3, 133.5, 133.2, 131.5, 129.7, 128.7), 128.4, 128.4, 127.3, 126.8, 124.8, 123.5, 119.6, 109.6, 104.2, 92.4, 55.8, 40.2, 36.2, 30.3; HRMS (ESI) calculated for $C_{25}H_{22}NO_2$ $(M+H)^+$ 368.1646, found 368.1650.



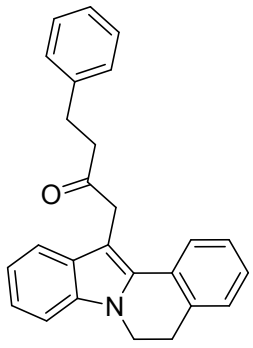
2-(2,3-dimethoxy-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)-1-phenylethanone (4h). White solid, mp 198.5-200.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.52 (ddd, *J* = 23.7, 15.0, 7.5 Hz, 4H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.10 (dd, *J* = 16.2, 8.6 Hz, 2H), 6.80 (s, 1H), 4.74 (s, 2H), 4.24 (t, *J* = 6.3 Hz, 2H), 3.91 (s, 3H), 3.60 (s, 3H), 3.07 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 148.2, 148.0, 137.0, 135.4, 133.2, 132.7, 129.2, 128.7, 128.4, 126.6, 121.9, 121.8, 119.5, 118.3, 111.5, 108.7, 108.7, 102.6, 56.0, 55.6, 40.3, 36.2, 29.7; HRMS (ESI) calculated for $C_{26}H_{24}NO_3$ $(M+H)^+$ 398.1751, found 398.1756.



1-(5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)propan-2-one (4i). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.40-7.33 (m, 2H), 7.31-7.23 (m, 3H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.27 (t, *J* = 6.3 Hz, 2H), 4.09 (s, 2H), 3.14 (t, *J* = 6.3 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 135.5, 133.8, 132.4, 129.2, 128.8, 128.5, 127.5, 125.4, 122.4, 119.8, 118.6, 109.0, 104.3, 41.3, 40.1, 30.1, 29.1; HRMS (ESI) calculated for $C_{19}H_{18}NO$ $(M+H)^+$ 276.1383, found 276.1387.

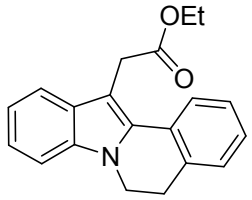


1-(5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)pentan-2-one (4j). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.39-7.33 (m, 2H), 7.32-7.22 (m, 4H), 7.15 (t, *J* = 7.4 Hz, 1H), 4.26 (t, *J* = 6.3 Hz, 2H), 4.08 (s, 2H), 3.13 (t, *J* = 6.3 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.64-1.49 (m, 3H), 0.82 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.0, 135.5, 133.8, 132.4, 129.2, 128.9, 128.5, 127.5, 127.4, 125.4, 122.3, 119.8, 118.6, 109.0, 104.3, 43.3, 40.7, 40.1, 30.1, 17.2, 13.7; HRMS (ESI) calculated for $C_{21}H_{22}NO$ $(M+H)^+$ 304.1696, found 304.1699.



1-(5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)-4-phenylbutan-2-one (4k). White

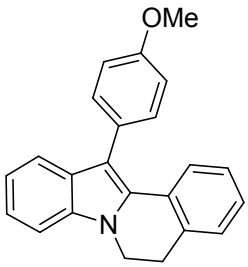
solid, mp 202.3-204.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.36-7.24 (m, 5H), 7.16 (dt, *J* = 14.7, 7.1 Hz, 4H), 7.05 (d, *J* = 7.4 Hz, 2H), 4.24 (t, *J* = 6.3 Hz, 2H), 4.07 (s, 2H), 3.11 (t, *J* = 6.3 Hz, 2H), 2.90-2.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 141.1, 135.5, 133.8, 132.4, 129.1, 128.8, 128.5, 128.4, 127.5, 127.4, 126.0, 125.4, 122.4, 119.8, 118.6, 109.0, 104.0, 42.8, 40.9, 40.1, 30.1, 29.8; HRMS (ESI) calculated for $C_{26}H_{24}NO$ $(M+H)^+$ 366.1853, found 366.1857.



ethyl 2-(5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)acetate (4l). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.30 (dd, *J* = 13.9, 6.7 Hz, 3H), 7.23 (d, *J* = 9.2 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.30-4.14 (m, 4H), 4.04 (s, 2H), 3.11 (t, *J* = 6.3 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 135.3, 134.0, 132.4, 129.3, 128.9, 128.4, 127.5, 127.4, 125.9, 122.2, 119.6, 119.2, 108.8, 103.9, 61.0, 40.1, 31.8, 30.2, 14.3; HRMS (ESI) calculated for $C_{20}H_{20}NO_2$ $(M+H)^+$ 306.1489, found 306.1493.

E. X-ray Crystallographic Data

Single Crystal X-ray Diffraction Data for compound 2g



X-ray structure determinations: Crystals of compound **2g** were obtained by slow evaporation of a mixture of n-pentane/acetone room temperature.
Crystal data for **2g**: **CCDC 1480918**

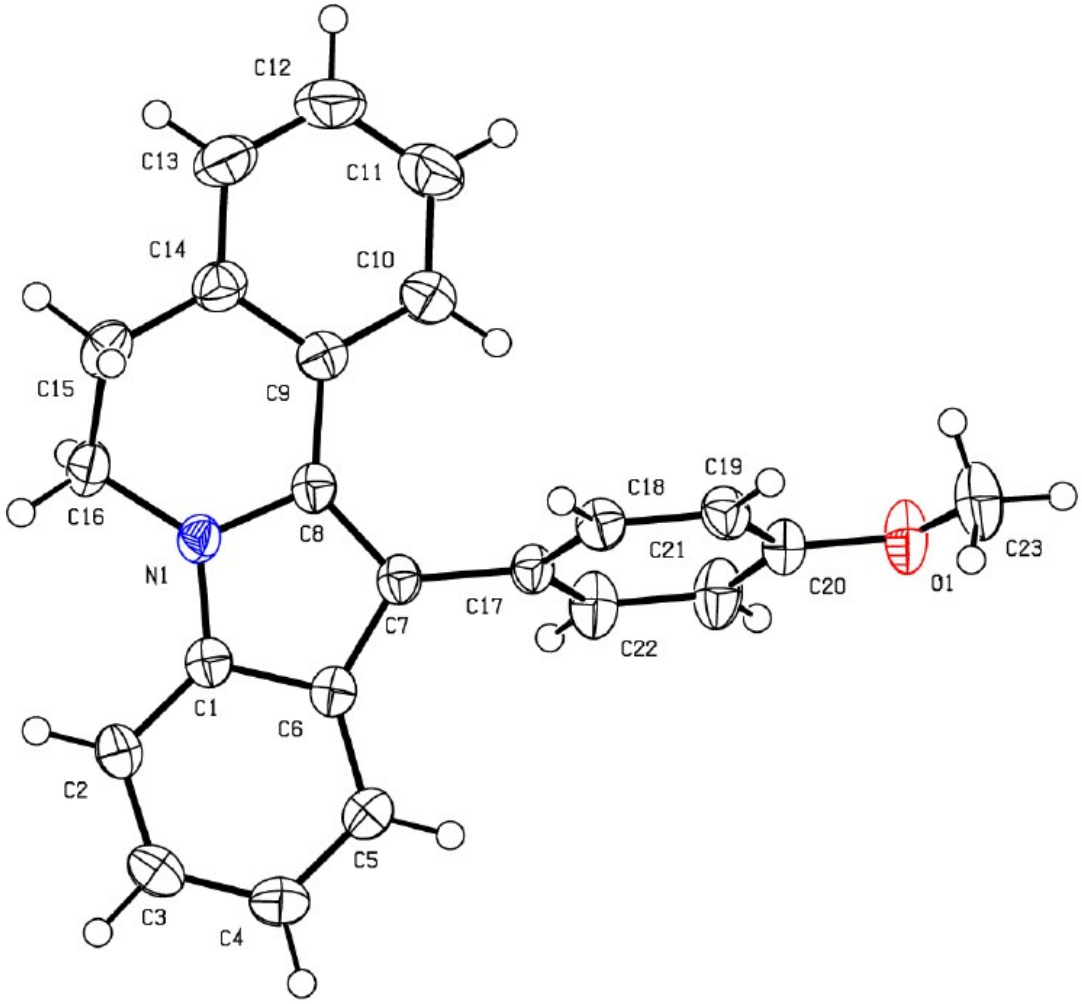
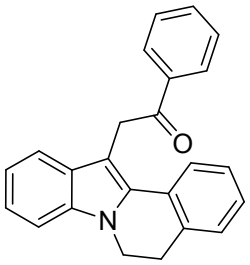


Table S1. Crystal data and structure refinement for CCDC 1480918.

Identification code	mo_60304b	
Empirical formula	C23 H19 N O	
Formula weight	325.39	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.9320(15) Å	a= 90°
	b = 6.9867(12) Å	b= 96.869(3)°
	c = 27.957(5) Å	g = 90°
Volume	1732.2(5) $Å^3$	
Z	4	
Density (calculated)	1.248 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	688	
Crystal size	0.700 x 0.700 x 0.480 mm^3	
Theta range for data collection	2.573 to 27.355°.	
Index ranges	$-8\leq h\leq 11$, $-9\leq k\leq 9$, $-36\leq l\leq 36$	
Reflections collected	11839	
Independent reflections	3876 [R(int) = 0.0275]	
Completeness to theta = 25.242°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.636	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3876 / 0 / 228	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R_1 = 0.0475, wR_2 = 0.1348	
R indices (all data)	R_1 = 0.0566, wR_2 = 0.1442	
Extinction coefficient	0.027(4)	
Largest diff. peak and hole	0.267 and -0.194 $e.Å^{-3}$	

Single Crystal X-ray Diffraction Data for compound 4a



X-ray structure determinations: Crystals of compound **4a** were obtained by slow evaporation of a mixture of n-pentane/acetone room temperature.

Crystal data for **4a**: **CCDC 1480927**

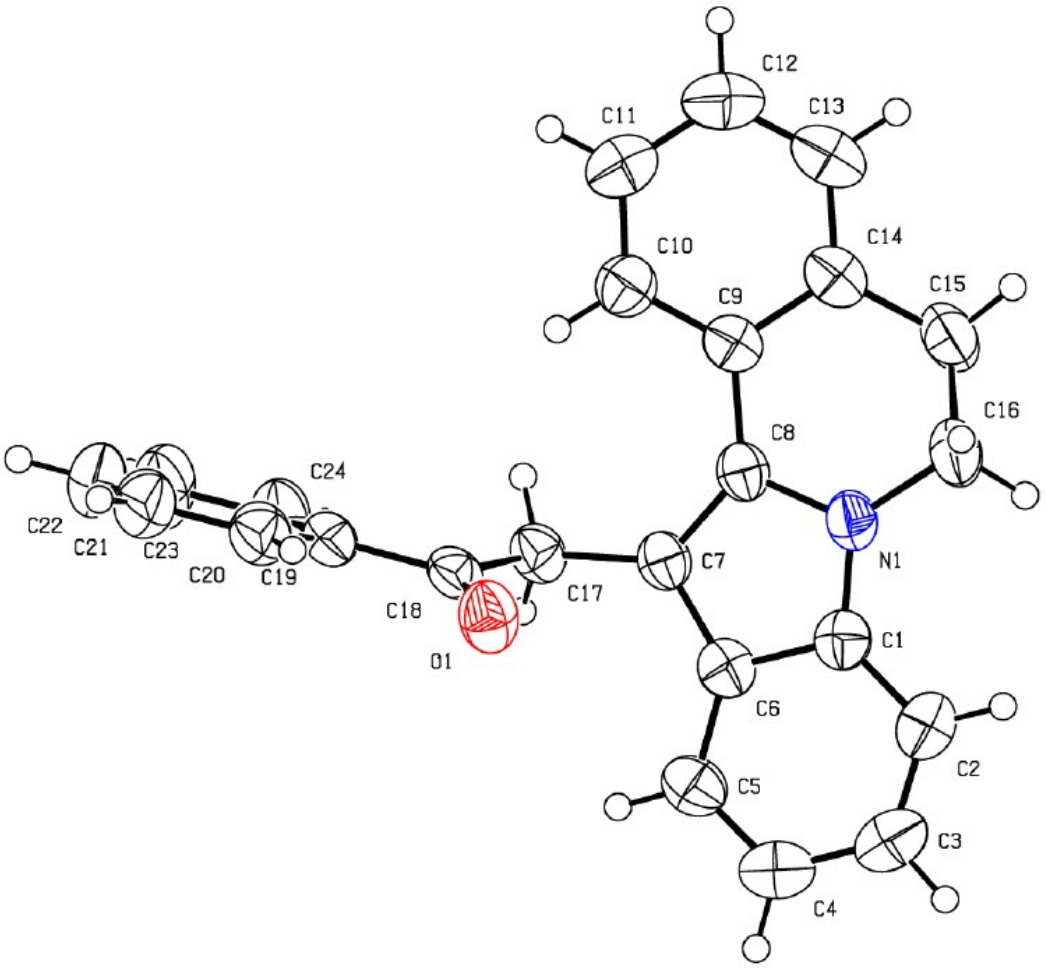
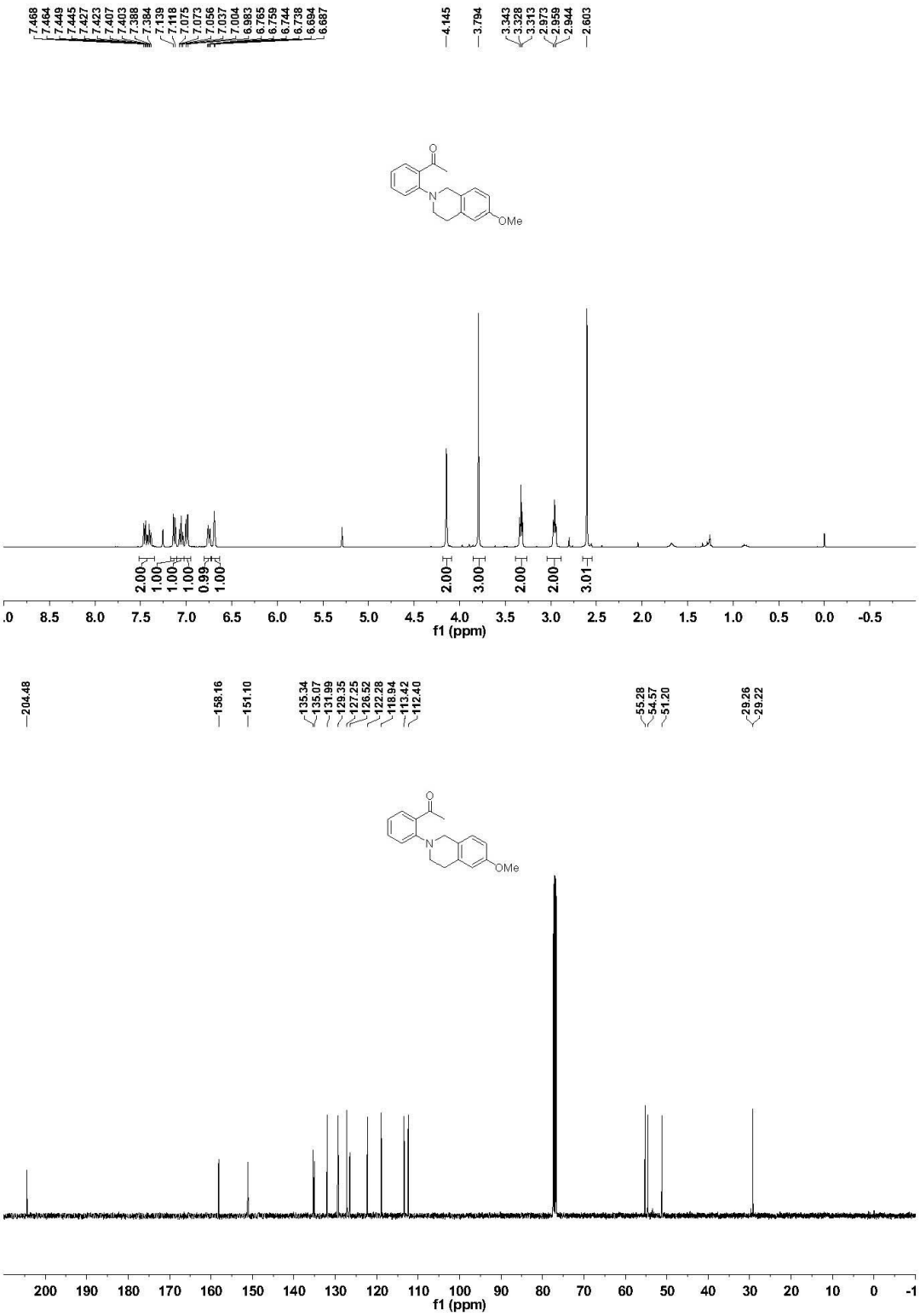


Table S2. Crystal data and structure refinement for CCDC 1480927.

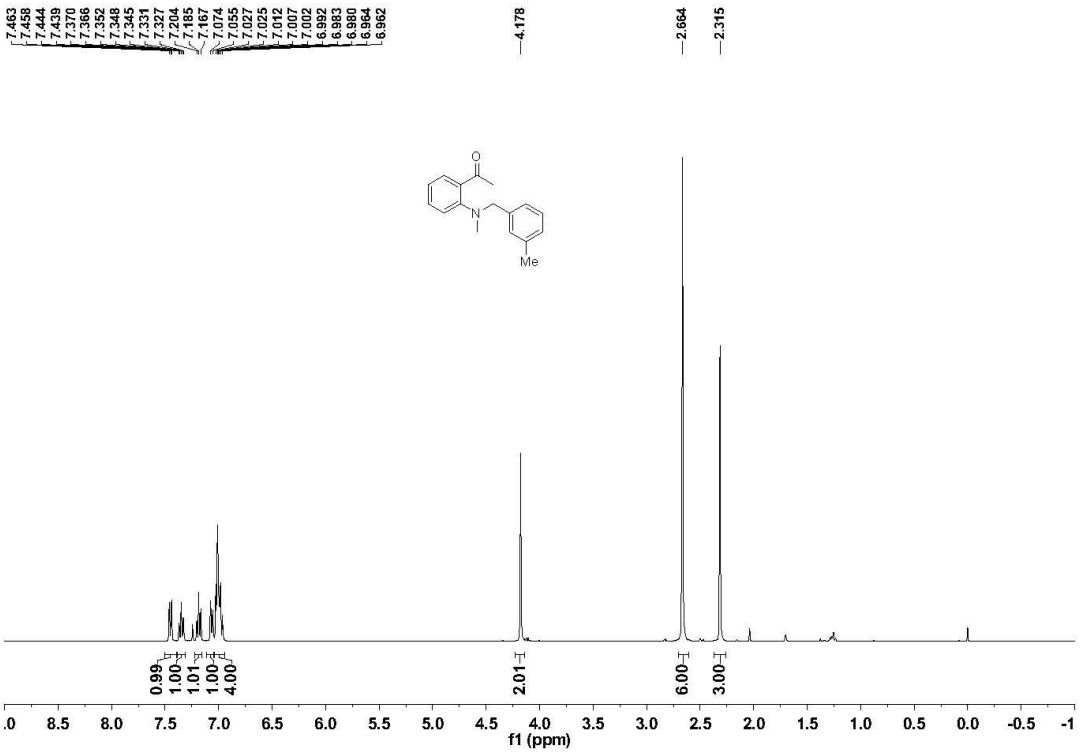
Identification code	a60105a	
Empirical formula	C24 H19 N O	
Formula weight	337.40	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.246(4) Å	a= 90°
	b = 21.733(10) Å	b= 99.084(6)°
	c = 8.690(4) Å	g = 90°
Volume	1724.3(14) $Å^3$	
Z	4	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	712	
Crystal size	0.700 x 0.080 x 0.050 mm^3	
Theta range for data collection	1.874 to 26.992°.	
Index ranges	$-11 \le h \le 11$, $-27 \le k \le 21$, $-10 \le l \le 10$	
Reflections collected	8321	
Independent reflections	3697 [R(int) = 0.0695]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.420	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3697 / 0 / 236	
Goodness-of-fit on F^2	0.931	
Final R indices [I>2sigma(I)]	R_1 = 0.0553, wR_2 = 0.1231	
R indices (all data)	R_1 = 0.0919, wR_2 = 0.1342	
Extinction coefficient	0.042(3)	
Largest diff. peak and hole	0.237 and -0.227 $e.Å^{-3}$	

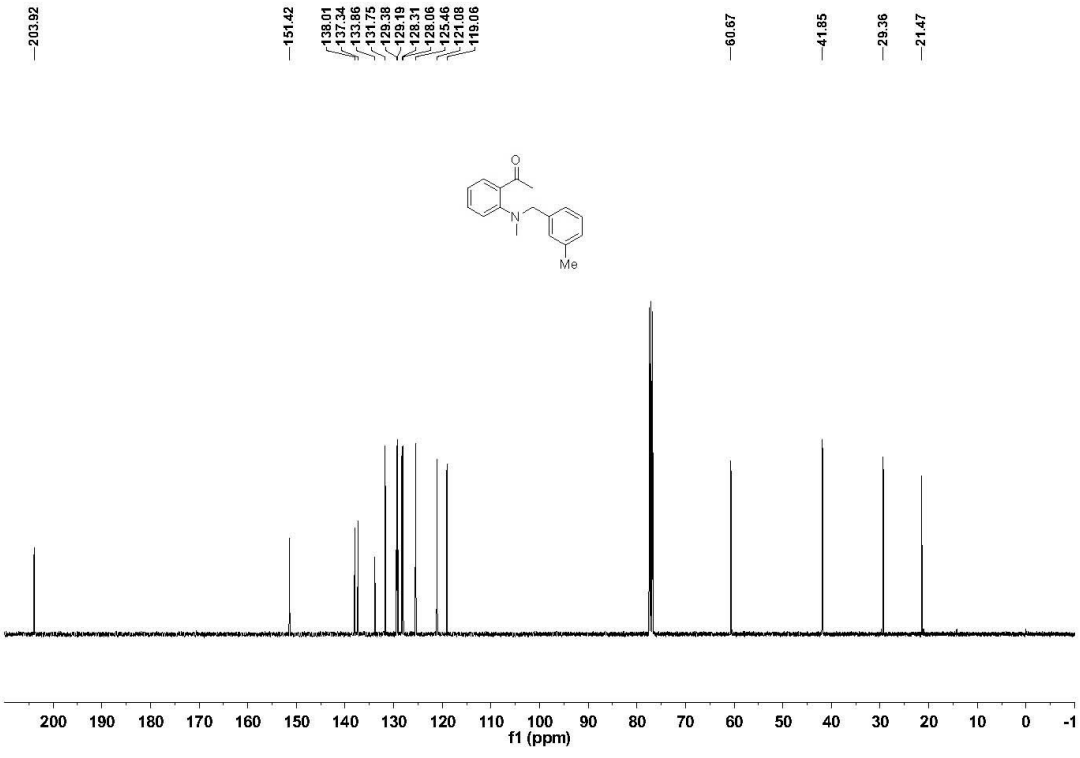
F: ^{1}H and ^{13}C NMR Spectra of Substrates

Compound 1c

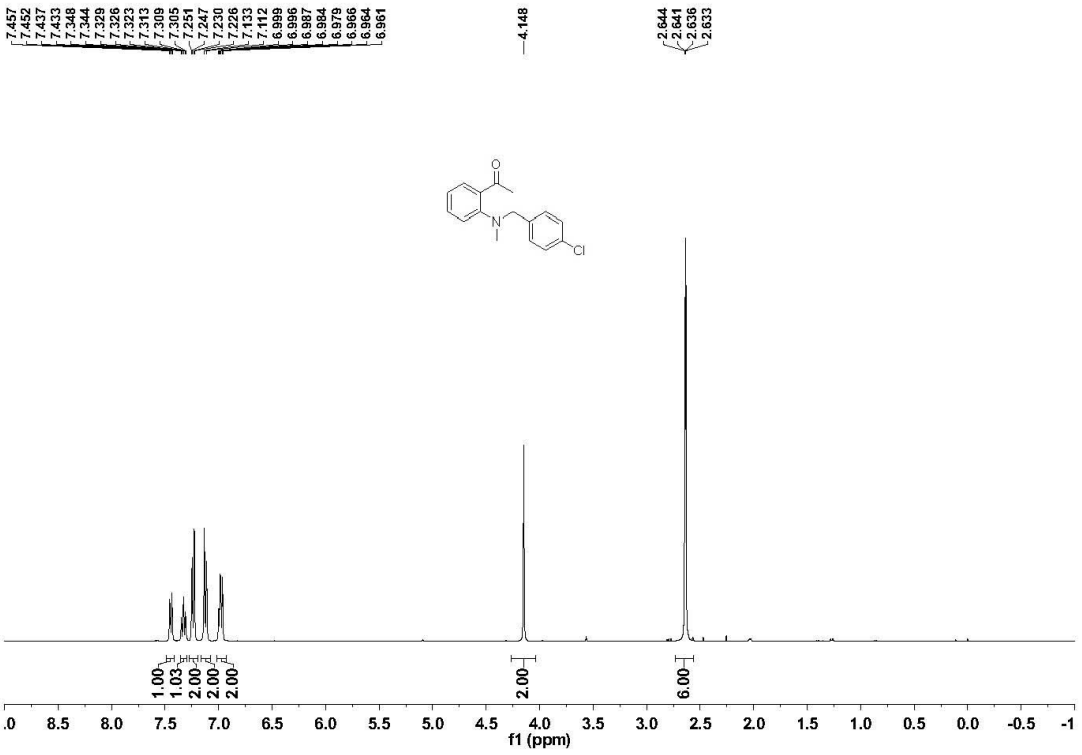


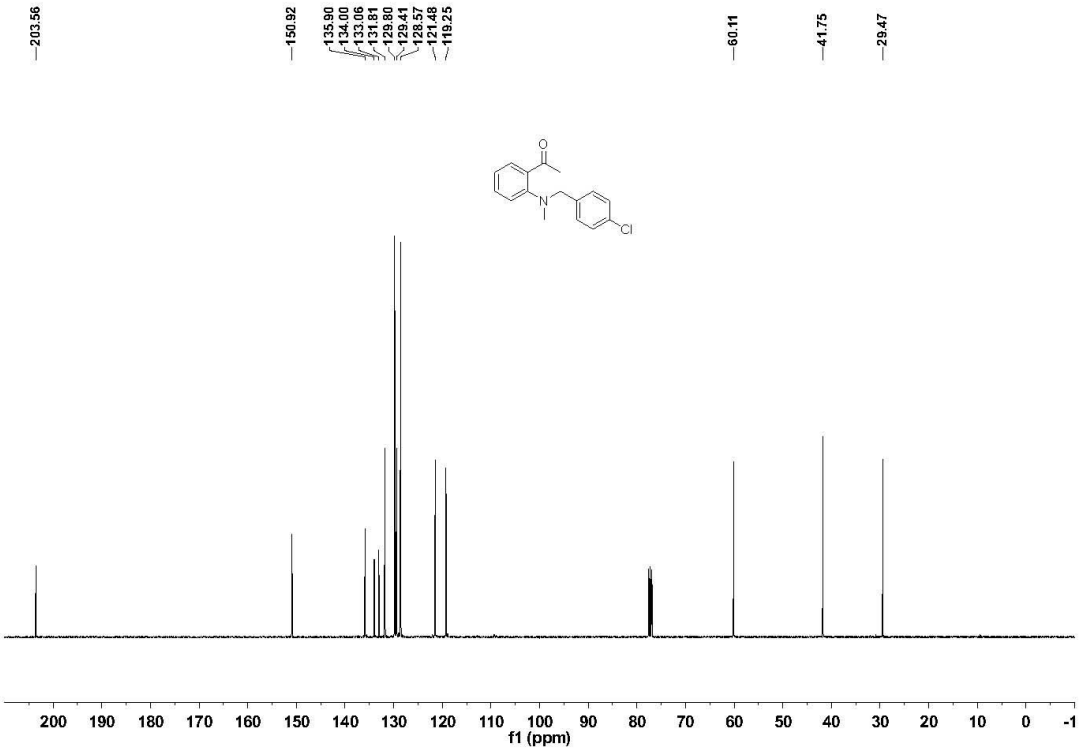
Compound 1m


7.463
7.458
7.444
7.439
7.370
7.366
7.352
7.348
7.345
7.331
7.327
7.204
7.185
7.167
7.074
7.055
7.027
7.025
7.012
7.007
7.002
6.992
6.983
6.980
6.964
6.962
4.178
2.664
2.315
O
N
Me
0.99
1.00
1.01
1.00
4.00
2.01
6.00
3.00
f1 (ppm)

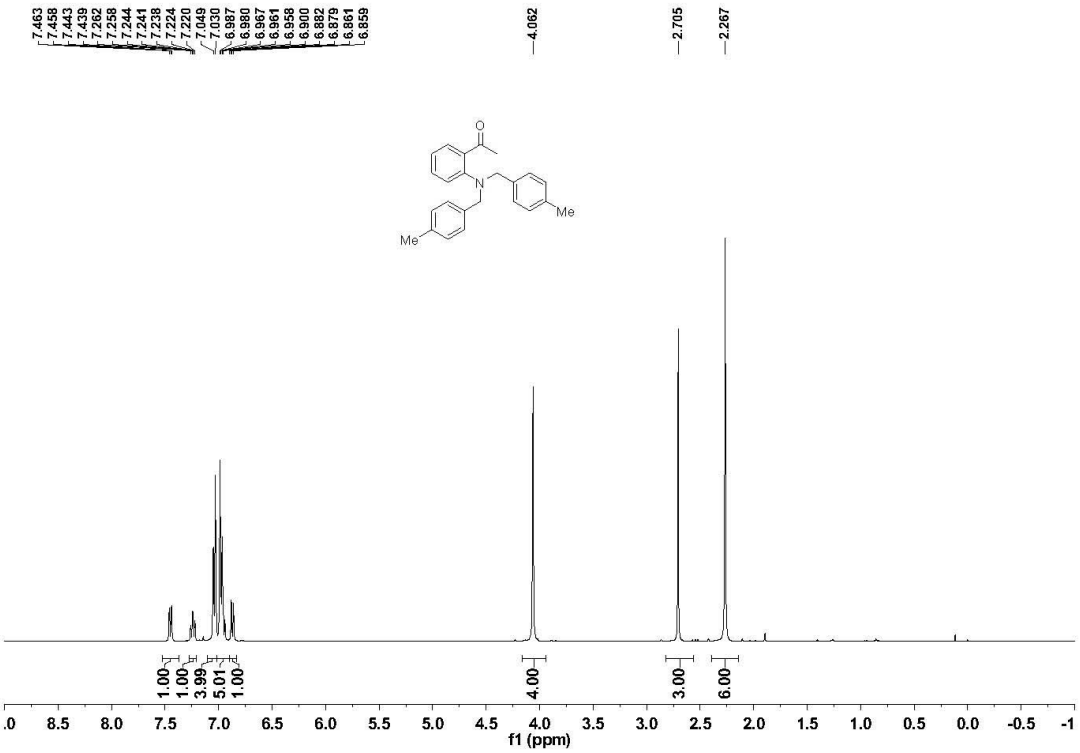

203.92
151.42
138.01
137.34
133.86
131.75
129.38
129.19
128.31
128.06
125.46
121.08
119.06
60.67
41.85
29.36
21.47
O
N
Me
f1 (ppm)

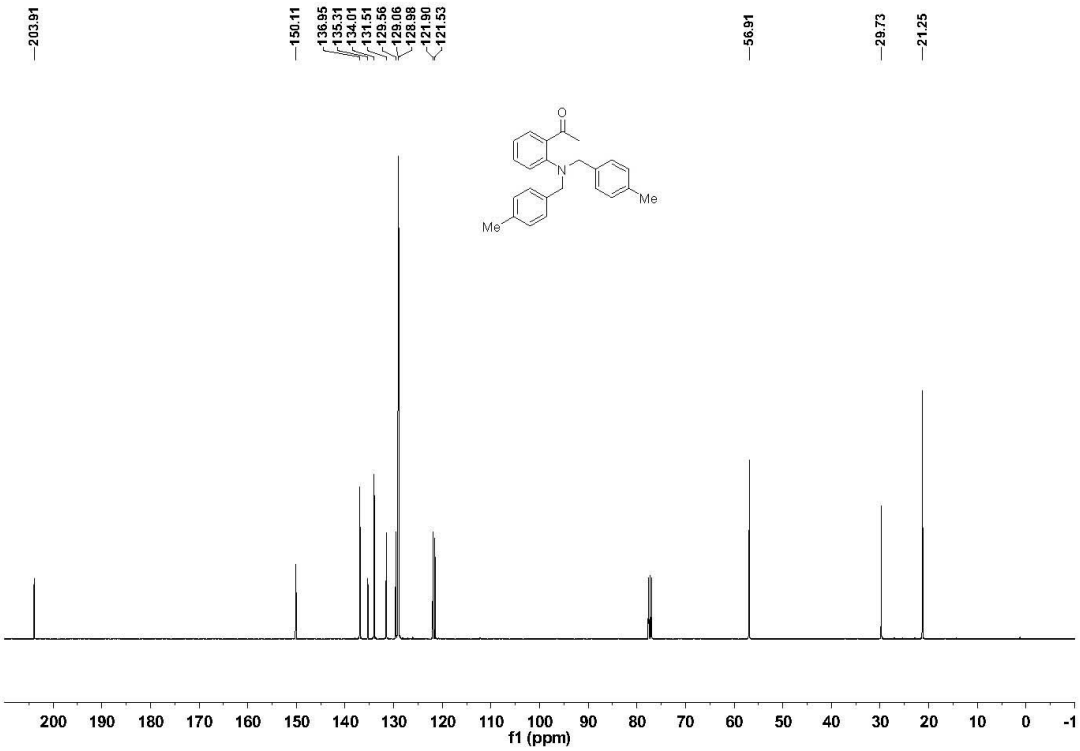
Compound 1n


7.457
7.452
7.437
7.433
7.348
7.344
7.329
7.326
7.323
7.313
7.309
7.305
7.251
7.247
7.230
7.226
7.133
7.112
6.999
6.996
6.987
6.984
6.979
6.966
6.964
6.961
4.148
2.644
2.641
2.636
2.633
O
N
Cl
1.00
1.03
2.00
2.00
2.00
2.00
6.00
f1 (ppm)

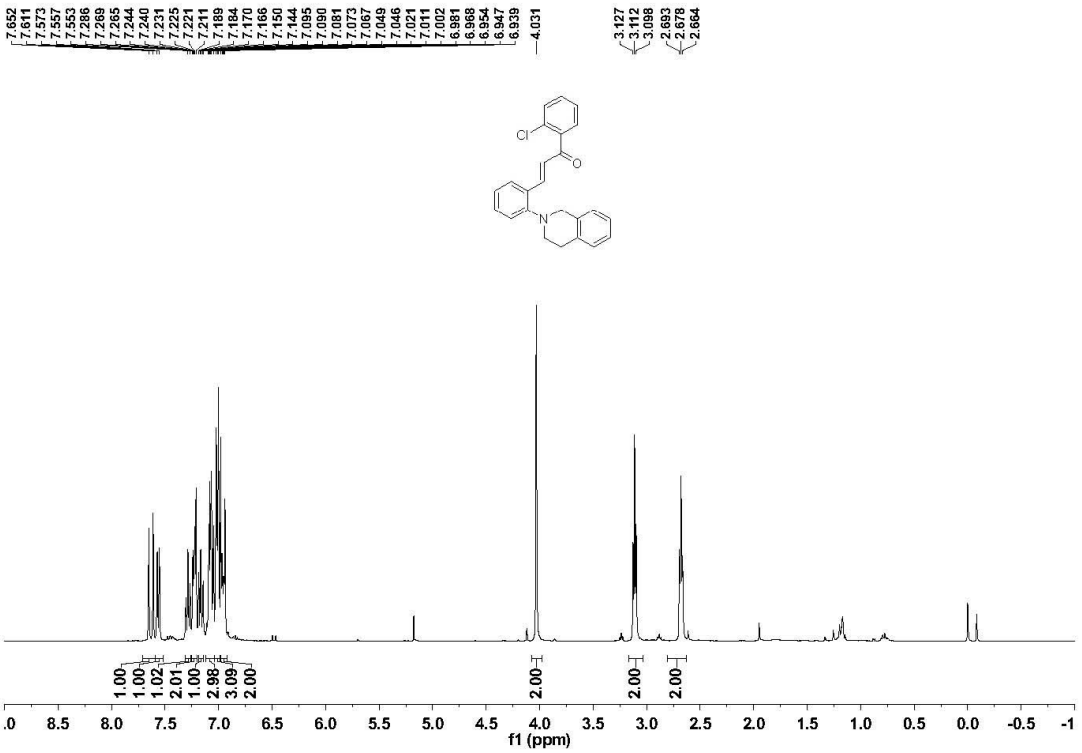

203.56
150.92
135.90
134.00
133.06
131.81
129.80
129.41
128.57
121.48
119.25
60.11
41.75
29.47
O
N
Cl
f1 (ppm)

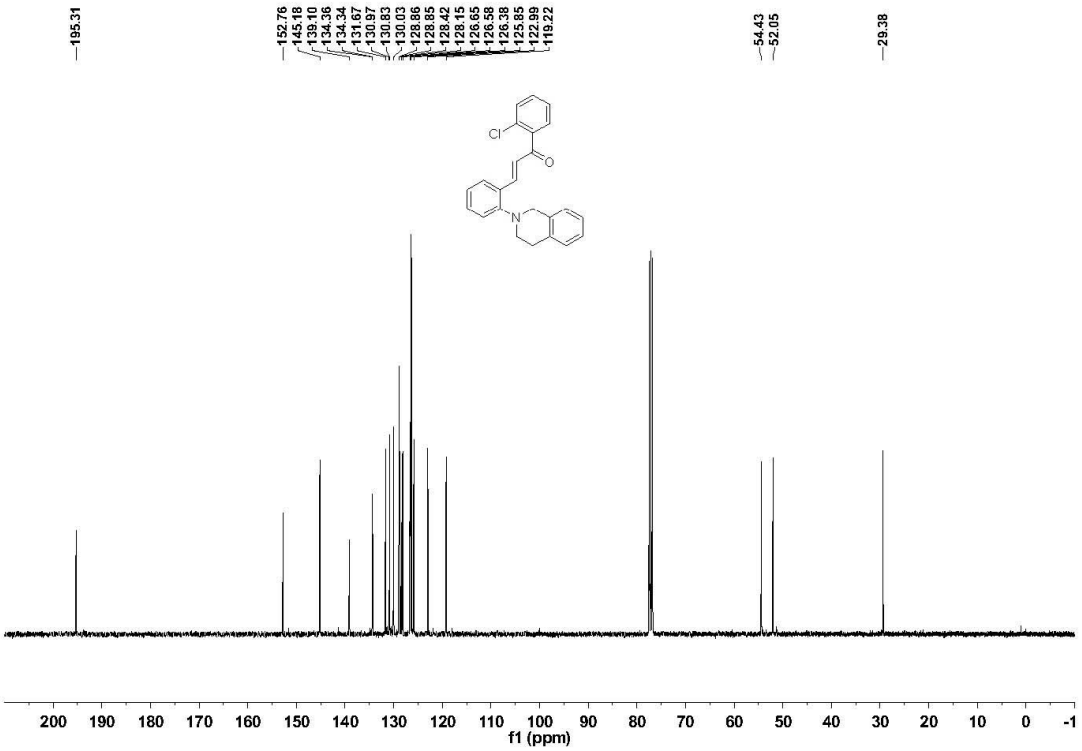
Compound 1q


7.463
7.458
7.443
7.439
7.262
7.258
7.244
7.241
7.238
7.224
7.220
7.049
7.030
6.987
6.980
6.967
6.961
6.958
6.900
6.882
6.879
6.861
6.859
4.062
2.705
2.267
O
N
Me
Me
1.00
1.00
3.99
5.01
1.00
4.00
3.00
6.00
f1 (ppm)

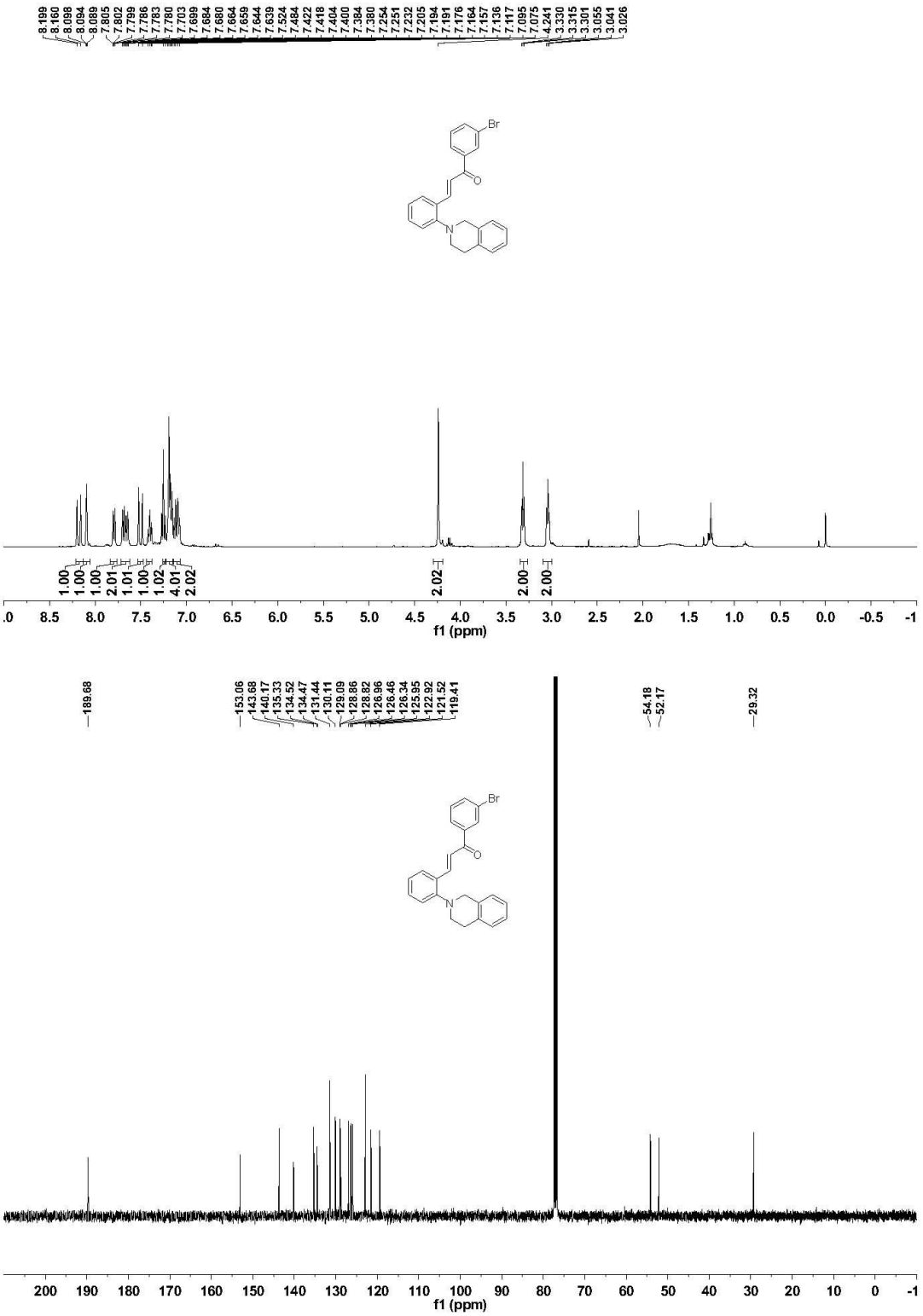

203.91
150.11
136.95
135.31
134.01
131.51
129.56
129.06
128.98
121.90
121.53
56.91
29.73
21.25
O
N
Me
Me
f1 (ppm)

Compound 3b

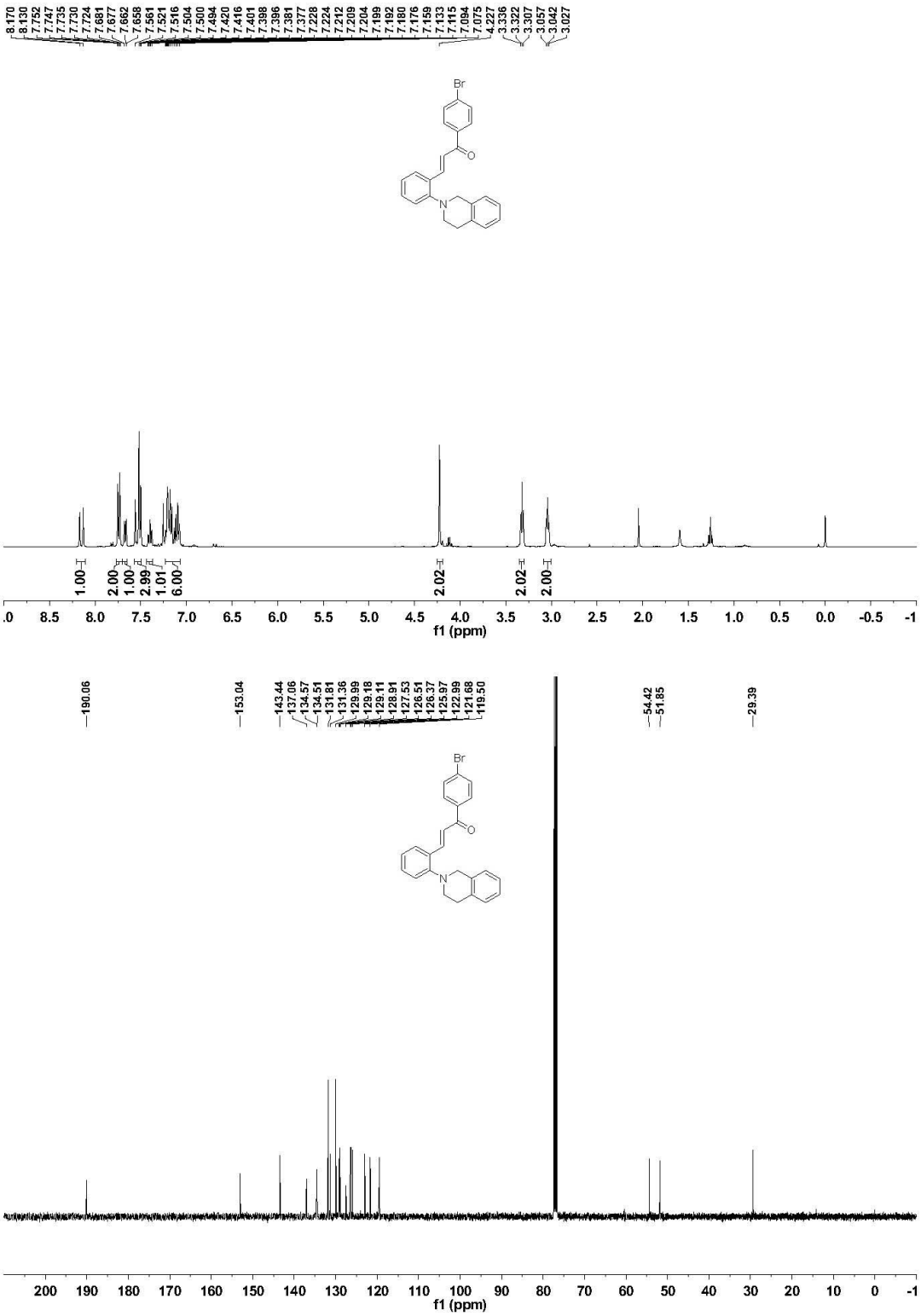

7.652
7.611
7.573
7.557
7.553
7.286
7.269
7.265
7.244
7.240
7.231
7.225
7.221
7.211
7.189
7.184
7.170
7.166
7.150
7.144
7.095
7.090
7.081
7.073
7.067
7.049
7.046
7.021
7.011
7.002
6.981
6.968
6.954
6.947
6.939
4.031
3.127
3.112
3.098
2.693
2.678
2.664
Cl
O
N
1.00
1.00
1.02
2.01
1.00
2.98
3.09
2.00
2.00
2.00
2.00
f1 (ppm)


195.31
152.76
145.18
139.10
134.36
134.34
131.67
130.97
130.83
130.03
128.86
128.85
128.42
128.15
126.65
126.58
126.38
125.85
122.99
119.22
54.43
52.05
29.38
Cl
O
N
f1 (ppm)

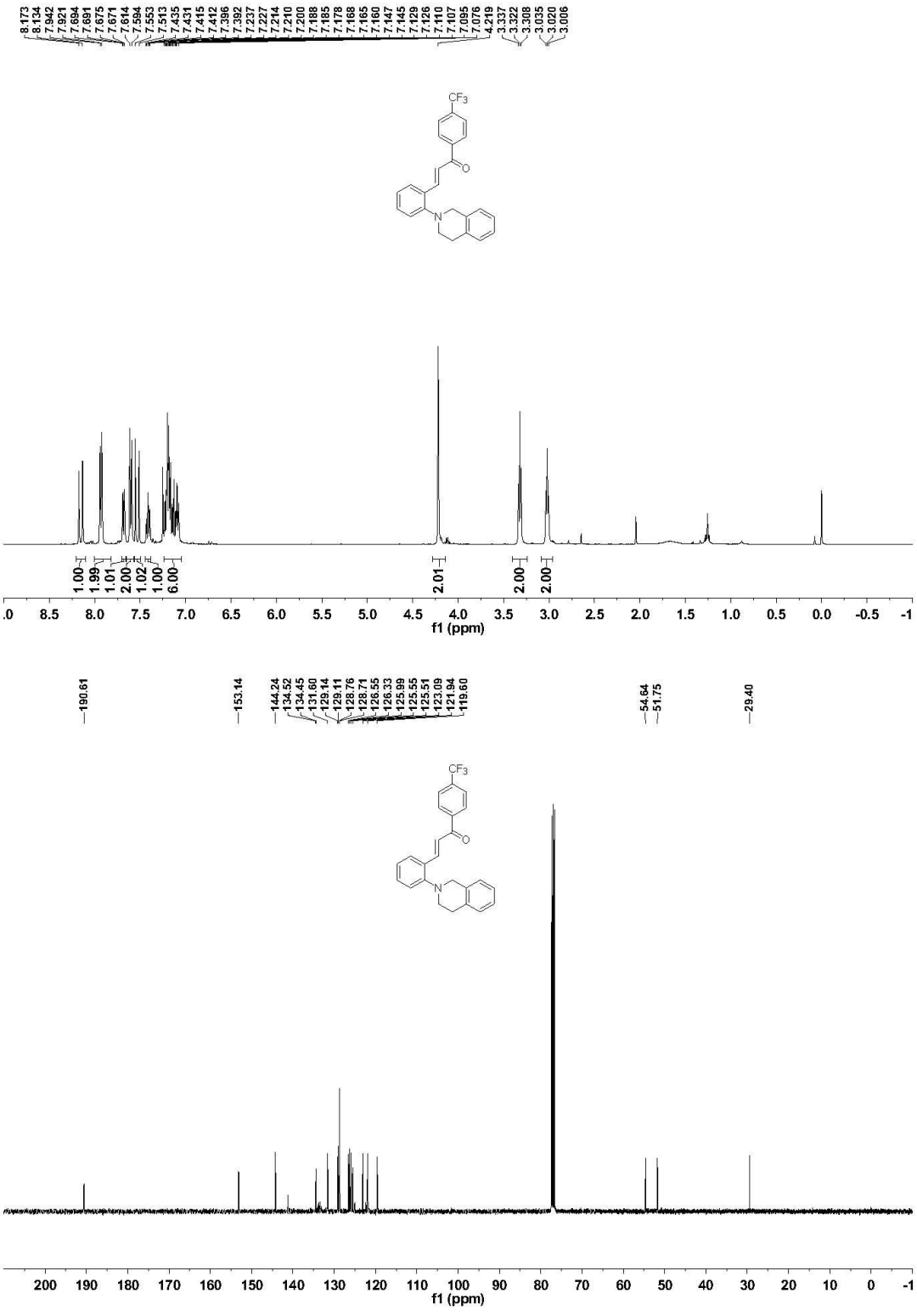
Compound 3c


8.199
8.160
8.098
8.094
8.089
7.805
7.802
7.799
7.786
7.783
7.780
7.703
7.699
7.684
7.680
7.664
7.659
7.644
7.639
7.524
7.484
7.422
7.418
7.404
7.400
7.384
7.380
7.254
7.251
7.232
7.205
7.194
7.191
7.176
7.164
7.157
7.136
7.117
7.095
7.075
4.241
3.330
3.315
3.301
3.055
3.041
3.026
Br
O
N
1.00
1.00
1.00
2.01
1.01
1.00
1.02
4.01
2.02
2.02
2.00
2.00
f1 (ppm)
189.68
153.06
143.68
140.17
135.33
134.52
134.47
131.44
130.11
129.09
128.86
128.82
126.96
126.46
126.34
125.95
122.92
121.52
119.41
54.18
52.17
29.32
Br
O
N
f1 (ppm)

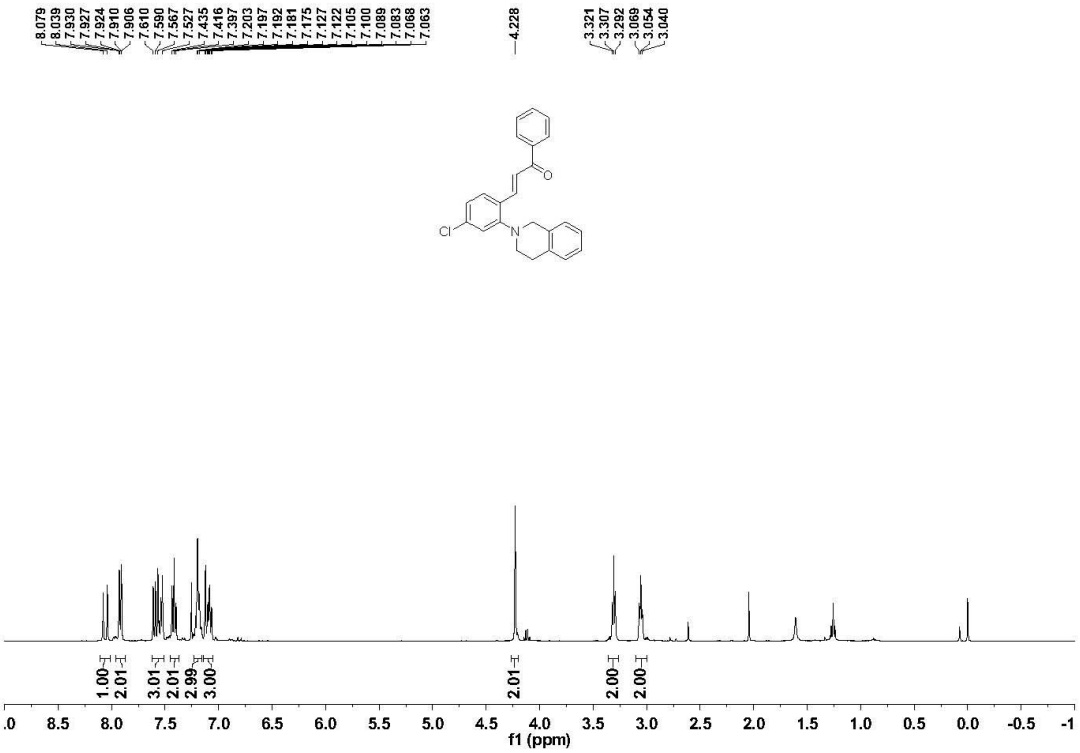
Compound 3d

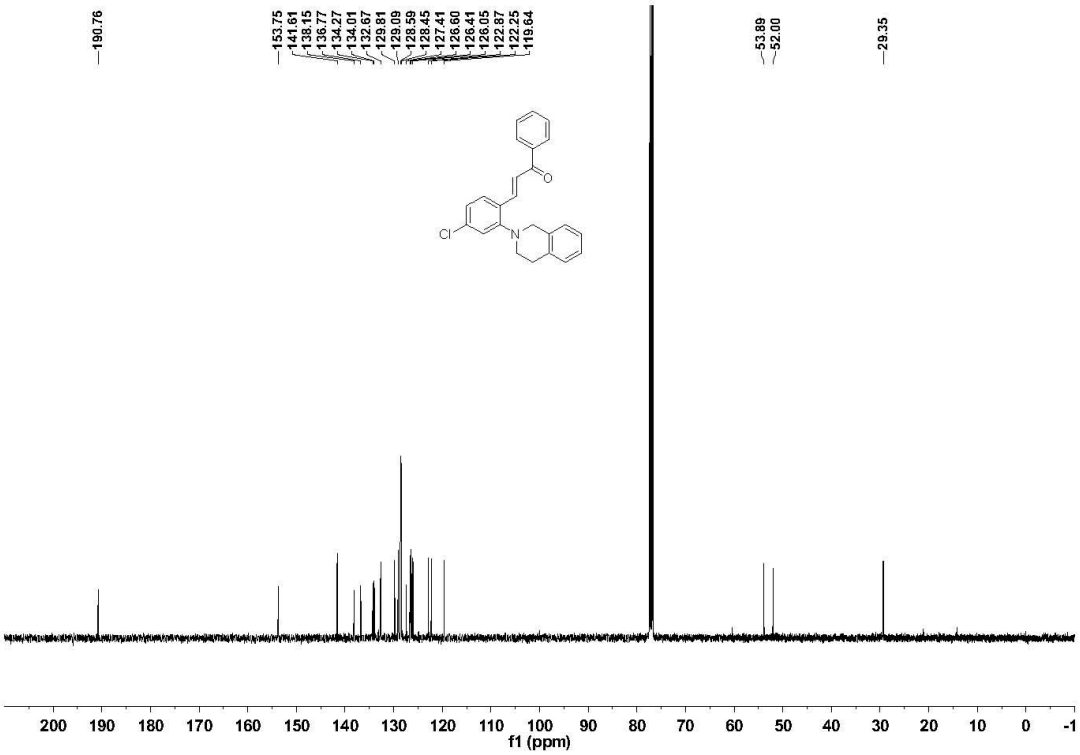

8.170
8.130
7.752
7.747
7.735
7.730
7.724
7.681
7.677
7.662
7.658
7.561
7.521
7.516
7.504
7.500
7.494
7.420
7.416
7.401
7.398
7.396
7.381
7.377
7.228
7.224
7.212
7.209
7.204
7.199
7.192
7.180
7.176
7.159
7.133
7.115
7.094
7.075
4.227
3.336
3.322
3.307
3.057
3.042
3.027
Br
O
N
1.00
2.00
1.00
2.99
1.01
6.00
2.02
2.02
2.00
f1 (ppm)
190.06
153.04
143.44
137.06
134.57
134.51
131.81
131.36
129.99
129.18
129.11
128.91
127.53
126.51
126.37
125.97
122.99
121.68
119.50
54.42
51.85
29.39
Br
O
N
f1 (ppm)

Compound 3e

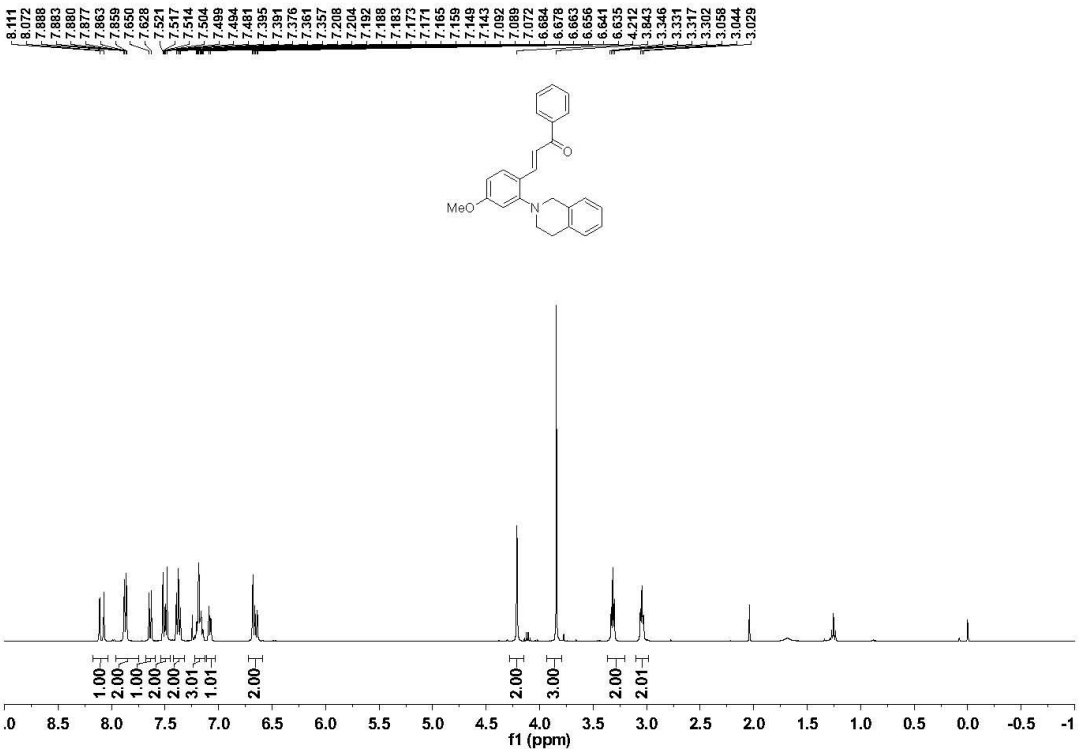

8.173
8.134
7.942
7.921
7.694
7.691
7.675
7.671
7.614
7.594
7.553
7.513
7.435
7.431
7.415
7.412
7.396
7.392
7.237
7.227
7.214
7.210
7.200
7.188
7.185
7.178
7.168
7.165
7.160
7.147
7.145
7.129
7.126
7.110
7.107
7.095
7.076
4.219
3.337
3.322
3.308
3.035
3.020
3.006
CF3
O
N
1.00
1.99
1.01
2.00
1.02
1.00
6.00
2.01
2.00
2.00
f1 (ppm)
190.61
153.14
144.24
134.52
134.45
131.60
129.14
129.11
128.76
128.71
126.55
126.33
125.99
125.55
125.51
123.09
121.94
119.60
54.64
51.75
29.40
CF3
O
N
f1 (ppm)

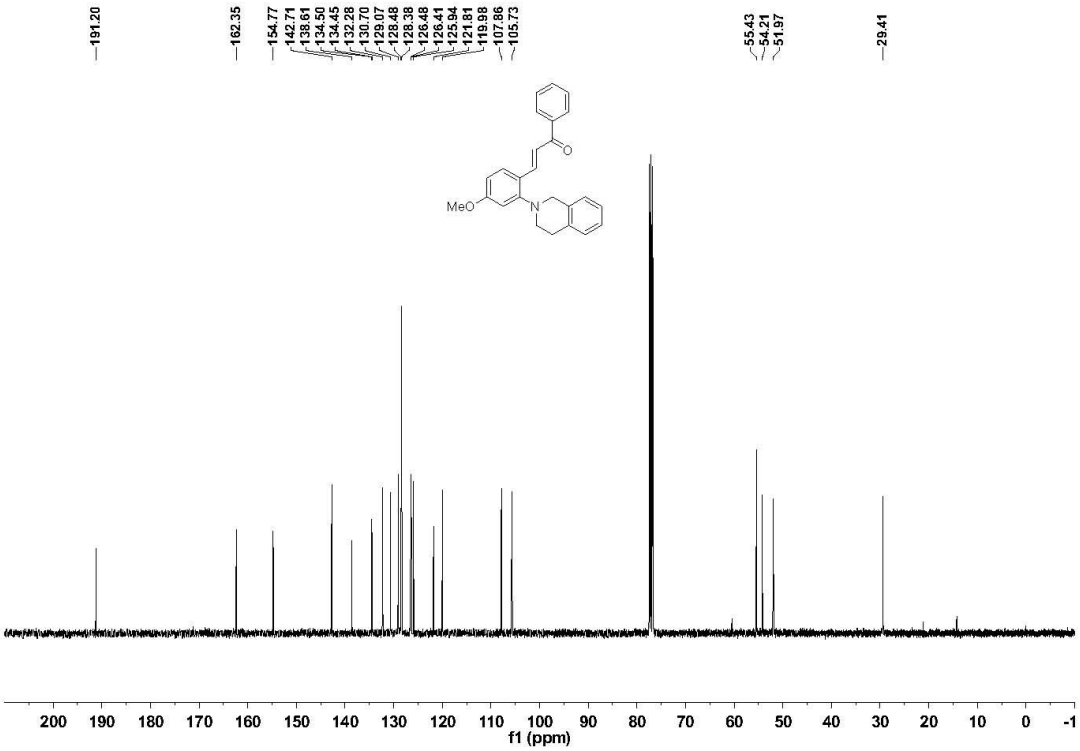
Compound 3f


8.079
8.039
7.930
7.927
7.924
7.910
7.906
7.610
7.590
7.567
7.527
7.435
7.416
7.397
7.203
7.197
7.192
7.181
7.175
7.127
7.122
7.105
7.100
7.089
7.083
7.068
7.063
4.228
3.321
3.307
3.292
3.069
3.054
3.040
Cl
O
N
1.00
2.01
3.01
2.01
2.99
3.00
2.01
2.00
2.00
f1 (ppm)

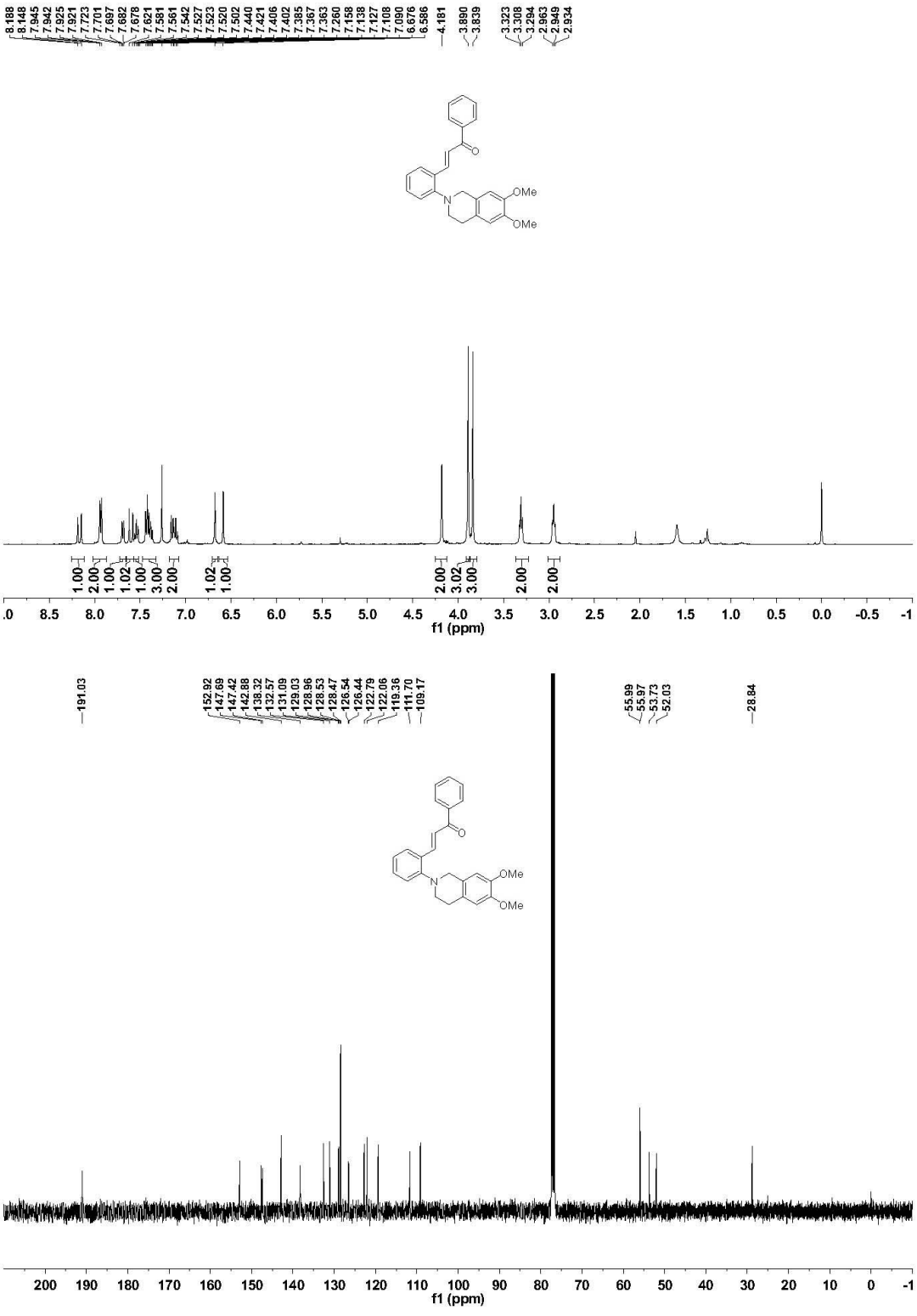

190.76
153.75
141.61
138.15
136.77
134.27
134.01
132.67
129.81
129.09
128.59
128.45
127.41
126.60
126.41
126.05
122.87
122.25
119.64
53.89
52.00
29.35
Cl
O
N
f1 (ppm)

Compound 3g

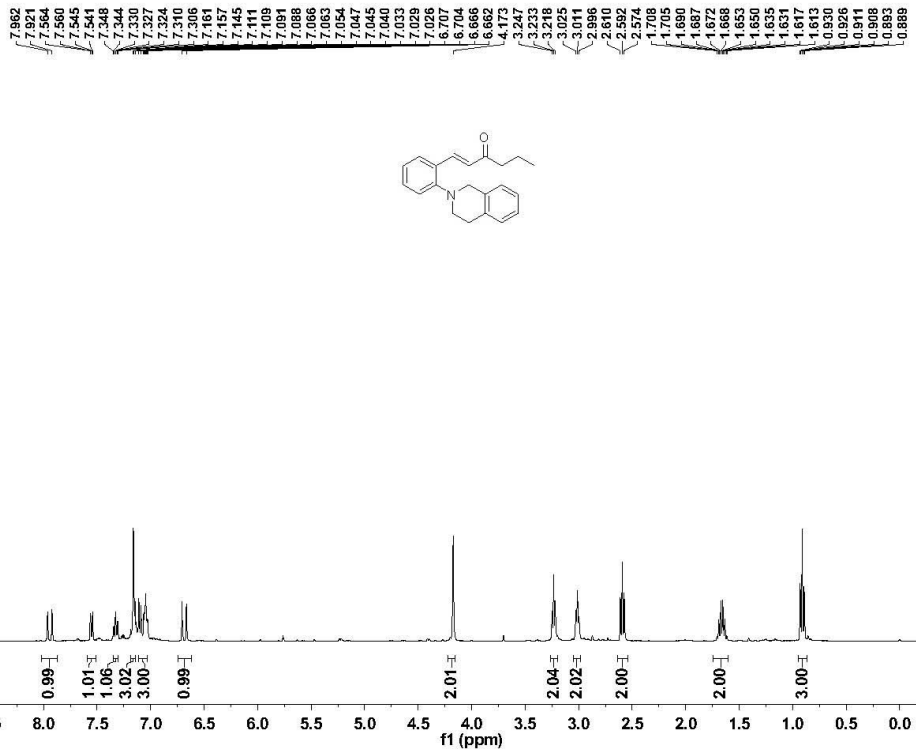

8.111
8.072
7.888
7.883
7.880
7.877
7.863
7.859
7.650
7.628
7.521
7.517
7.514
7.504
7.499
7.494
7.481
7.395
7.391
7.376
7.361
7.357
7.208
7.204
7.192
7.188
7.183
7.173
7.171
7.165
7.159
7.149
7.143
7.092
7.089
7.072
6.684
6.678
6.663
6.656
6.641
6.635
4.212
3.843
3.346
3.331
3.317
3.302
3.058
3.044
3.029
MeO
N
O
1.00
2.00
1.00
2.00
2.00
3.01
1.01
2.00
2.00
3.00
2.00
2.01
f1 (ppm)

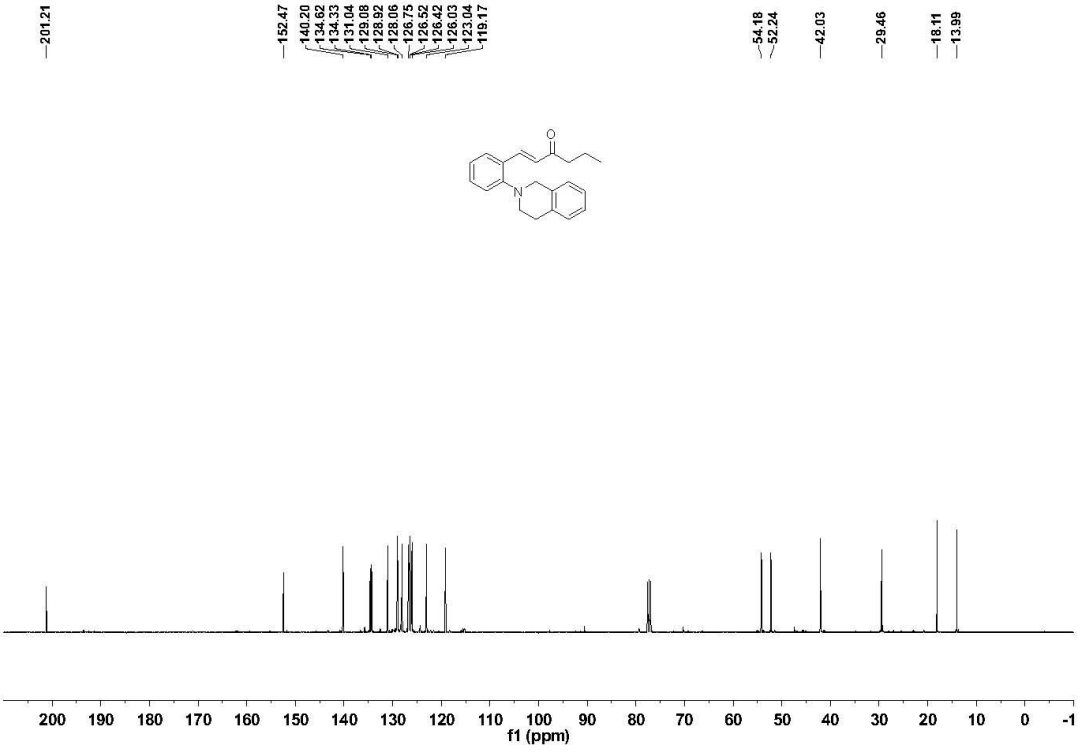

191.20
162.35
154.77
142.71
138.61
134.50
134.45
132.28
130.70
129.07
128.48
128.38
126.48
126.41
125.94
121.81
119.98
107.86
105.73
55.43
54.21
51.97
29.41
MeO
N
O
f1 (ppm)

Compound 3h

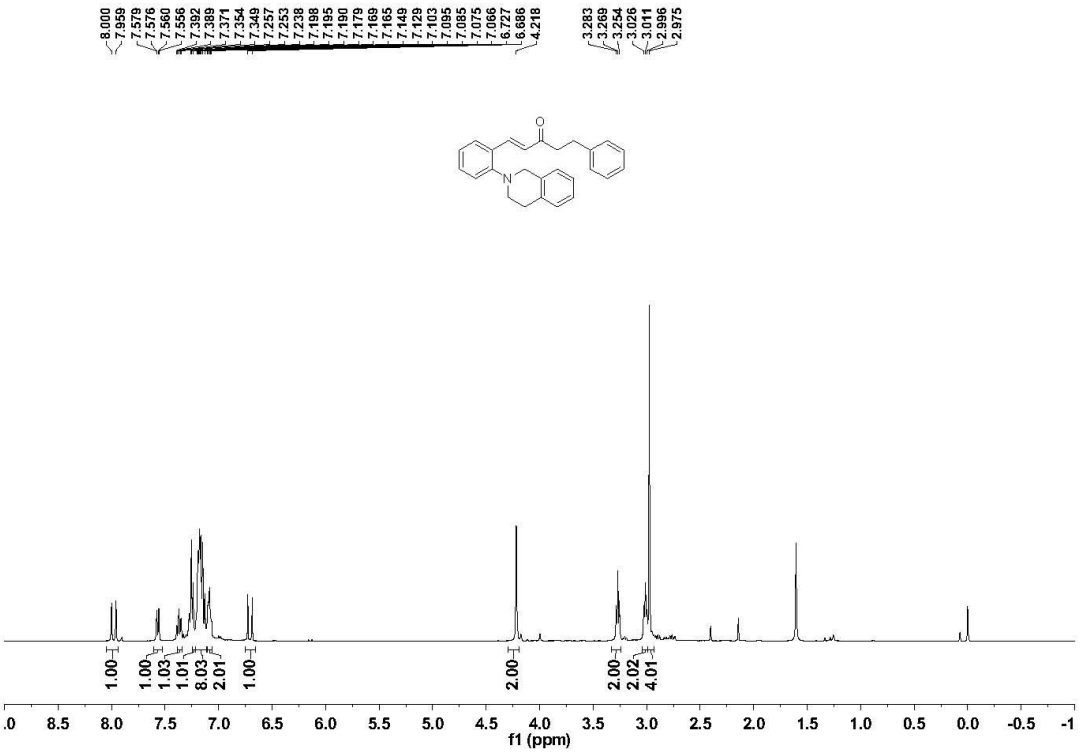

8.188
8.148
7.945
7.942
7.925
7.921
7.723
7.701
7.697
7.682
7.678
7.621
7.581
7.561
7.542
7.527
7.523
7.520
7.502
7.440
7.421
7.406
7.402
7.385
7.367
7.363
7.260
7.158
7.138
7.127
7.108
7.090
6.676
6.586
4.181
3.890
3.839
3.323
3.308
3.294
2.963
2.949
2.934
OMe
OMe
1.00
2.00
1.00
1.02
1.00
3.00
2.00
1.02
1.00
2.00
3.02
3.00
2.00
2.00
f1 (ppm)
191.03
152.92
147.69
147.42
142.88
138.32
132.57
131.09
129.03
128.96
128.53
128.47
126.54
126.44
122.79
122.06
119.36
111.70
109.17
55.99
55.97
53.73
52.03
28.84
OMe
OMe
f1 (ppm)

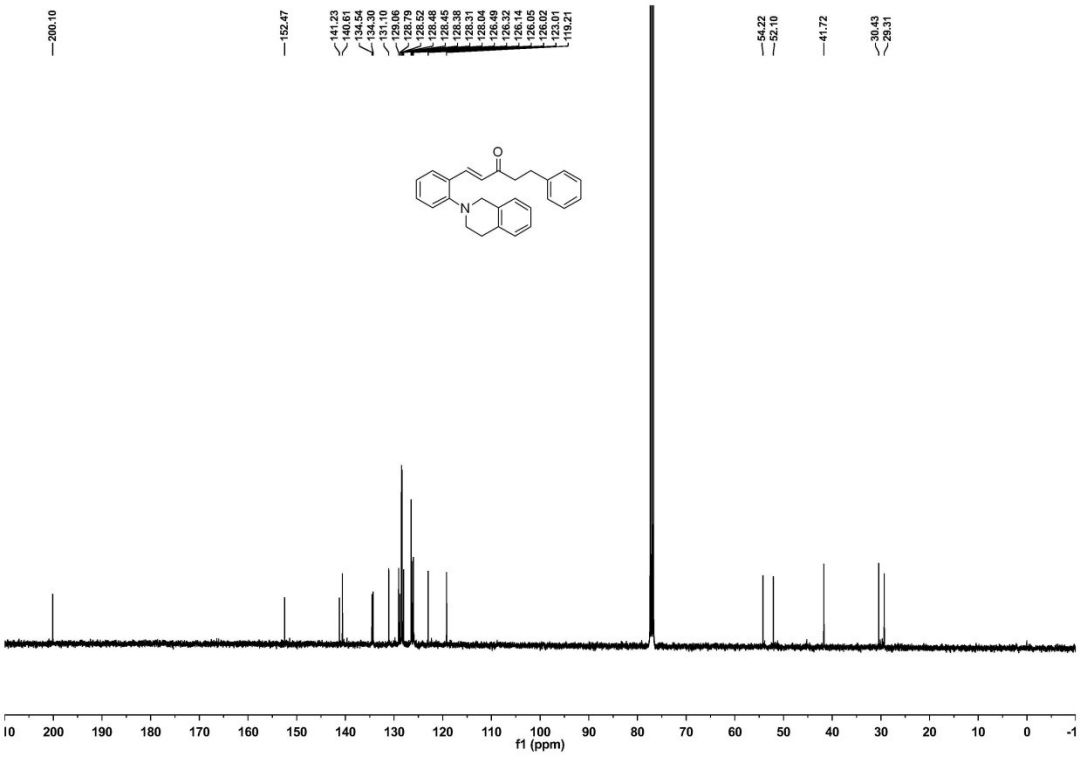
Compound 3j


7.962
7.921
7.564
7.560
7.545
7.541
7.348
7.344
7.330
7.327
7.324
7.310
7.306
7.161
7.157
7.145
7.111
7.109
7.091
7.088
7.066
7.063
7.054
7.047
7.045
7.040
7.033
7.029
7.026
6.707
6.704
6.666
6.662
4.173
3.247
3.233
3.218
3.025
3.011
2.996
2.610
2.592
2.574
1.708
1.705
1.690
1.687
1.672
1.668
1.653
1.650
1.635
1.631
1.617
1.613
0.930
0.926
0.911
0.908
0.893
0.889
O
N
0.99
1.01
1.06
3.02
3.00
0.99
2.01
2.04
2.02
2.00
2.00
3.00
f1 (ppm)

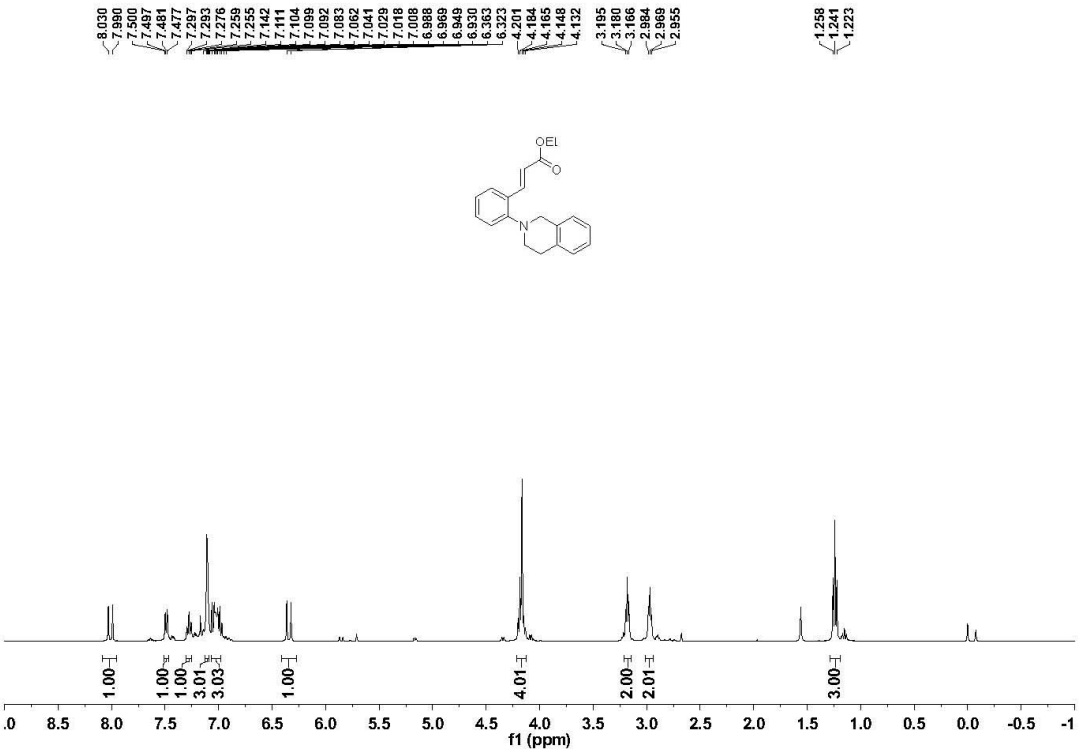

201.21
152.47
140.20
134.82
134.33
131.04
129.08
128.92
128.06
126.75
126.52
126.42
126.03
123.04
119.17
54.18
52.24
42.03
29.46
18.11
13.99
O
N
f1 (ppm)

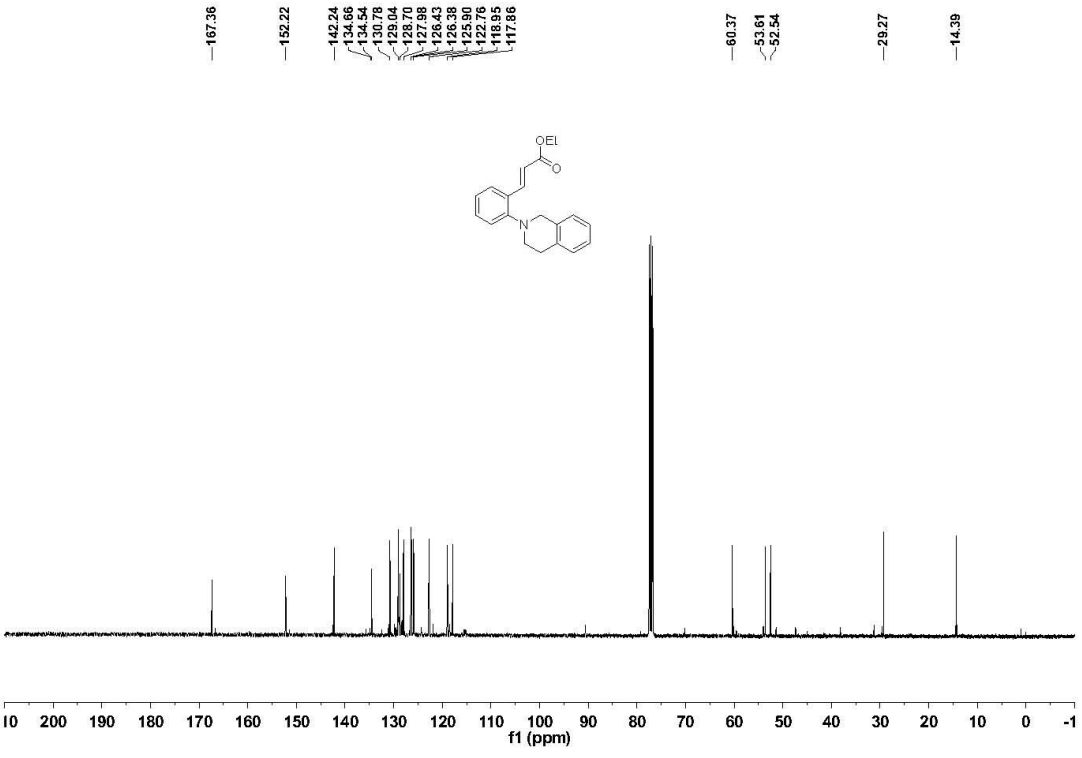
Compound 3k


8.000
7.959
7.579
7.576
7.560
7.556
7.392
7.389
7.371
7.354
7.349
7.257
7.253
7.238
7.198
7.195
7.190
7.179
7.169
7.165
7.149
7.129
7.103
7.095
7.085
7.075
7.066
6.727
6.686
4.218
3.283
3.269
3.254
3.026
3.011
2.996
2.975
O
N
1.00
1.00
1.03
1.01
8.03
2.01
1.00
2.00
2.00
2.02
4.01
f1 (ppm)


200.10
152.47
141.23
140.61
134.54
134.30
131.10
129.06
128.79
128.52
128.46
128.45
128.38
128.31
128.04
126.49
126.32
126.14
126.05
125.92
123.01
119.21
54.22
52.10
41.72
30.43
29.31
O
N
f1 (ppm)

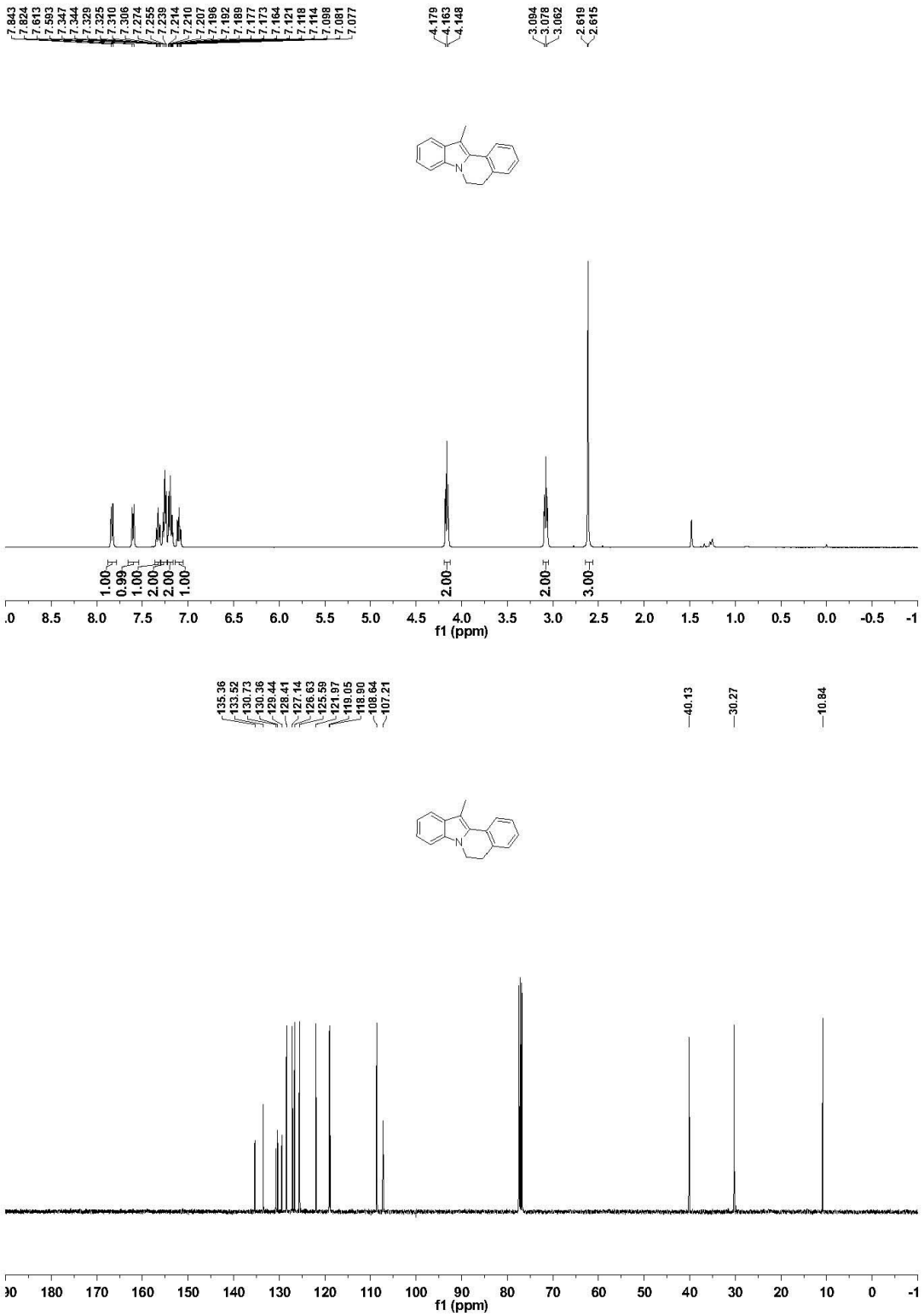
Compound 3l


8.030
7.990
7.500
7.497
7.481
7.477
7.297
7.293
7.276
7.259
7.255
7.142
7.111
7.104
7.099
7.092
7.083
7.062
7.041
7.029
7.018
7.008
6.988
6.969
6.949
6.930
6.363
6.323
4.201
4.184
4.165
4.148
4.132
3.195
3.180
3.166
2.984
2.969
2.955
1.258
1.241
1.223
OEt
O
N
1.00
1.00
1.00
3.01
3.03
1.00
4.01
2.00
2.01
3.00
f1 (ppm)

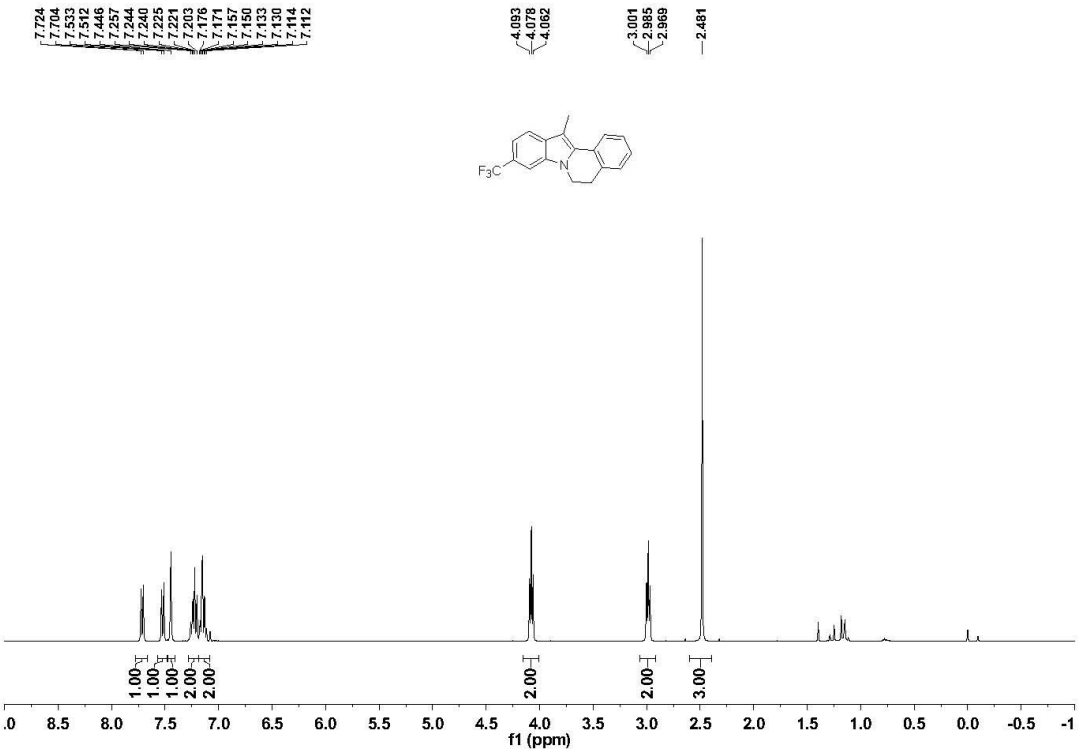

167.36
152.22
142.24
134.66
134.54
130.78
129.04
128.70
127.98
126.43
126.38
125.90
122.76
118.95
117.86
60.37
53.61
52.54
29.27
14.39
OEt
O
N
f1 (ppm)

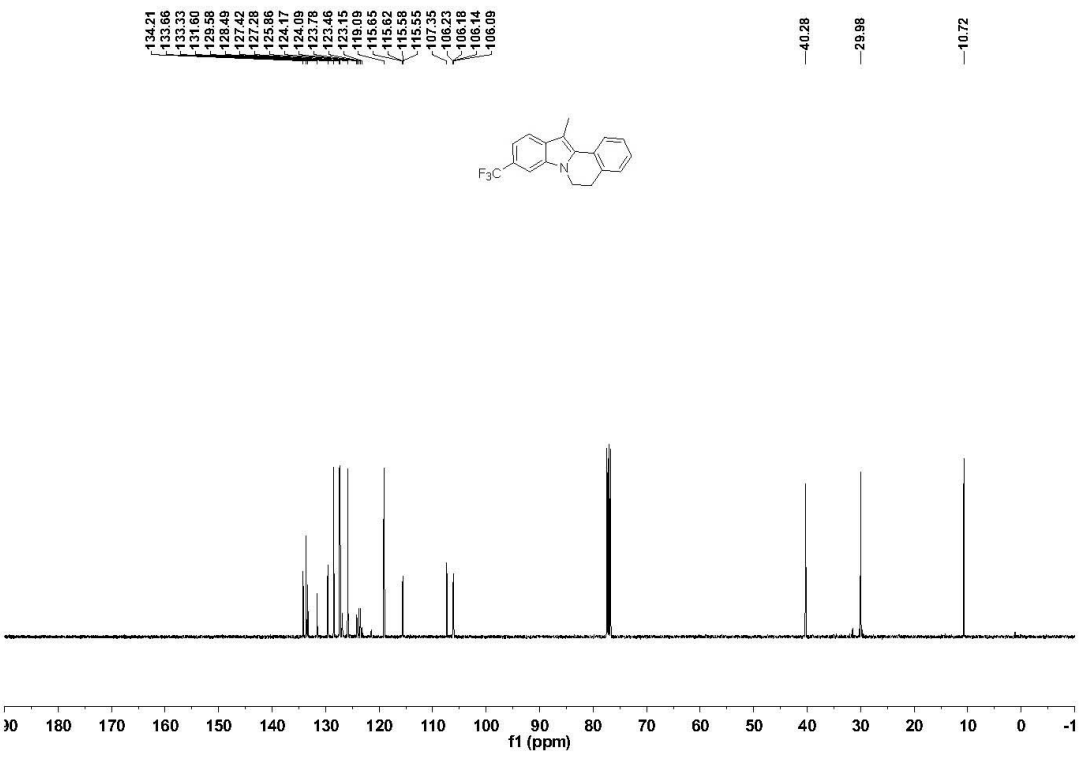
G: ^{1}H and ^{13}C NMR Spectra of Products

Compound 2a

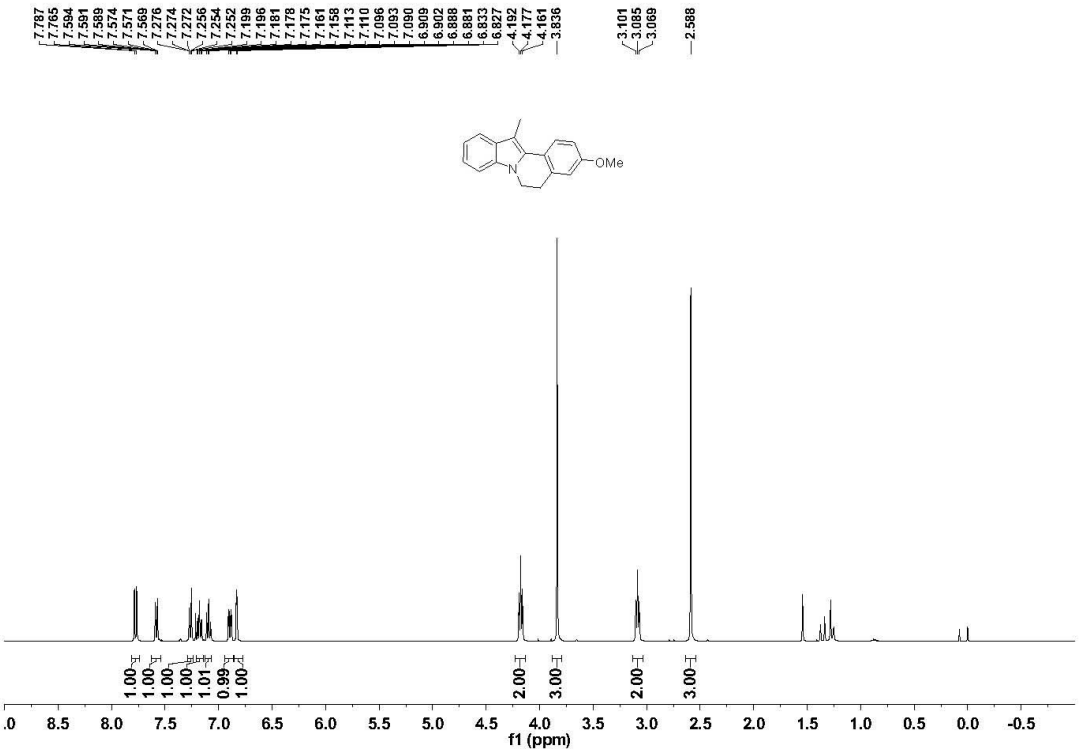


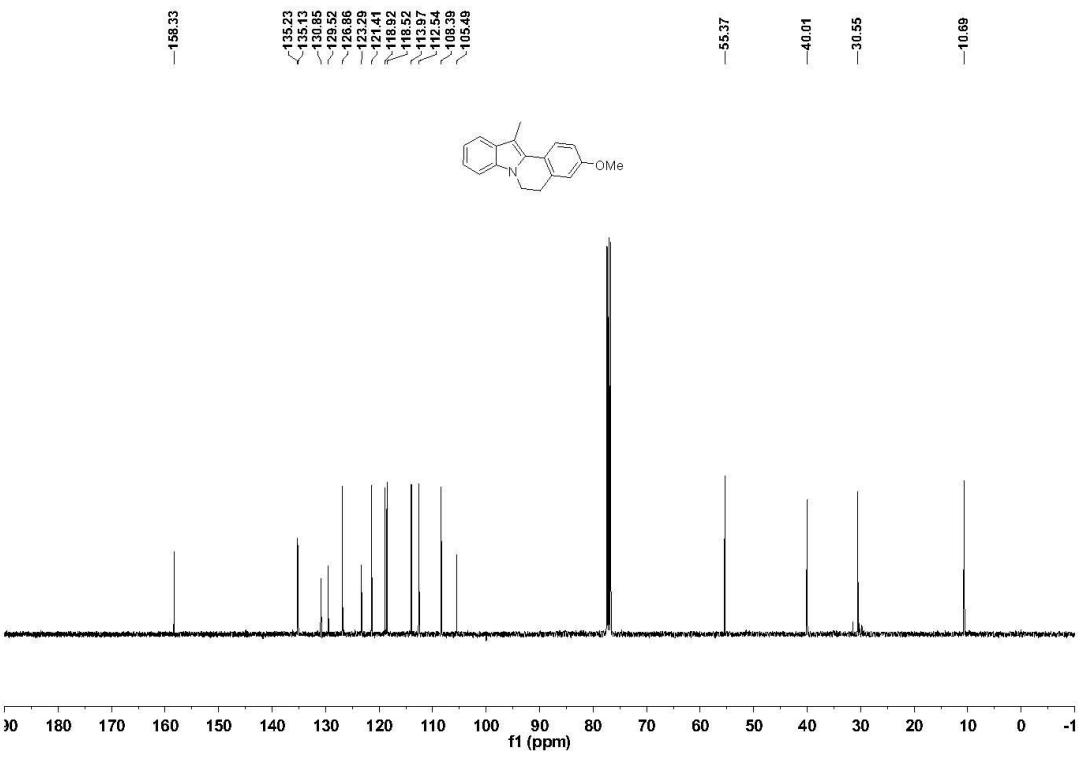
Compound 2b


7.724
7.704
7.533
7.512
7.446
7.257
7.244
7.240
7.225
7.221
7.203
7.176
7.171
7.157
7.150
7.133
7.130
7.114
7.112
4.093
4.078
4.062
3.001
2.985
2.969
2.481
F3C
1.00
1.00
1.00
2.00
2.00
2.00
2.00
3.00
f1 (ppm)

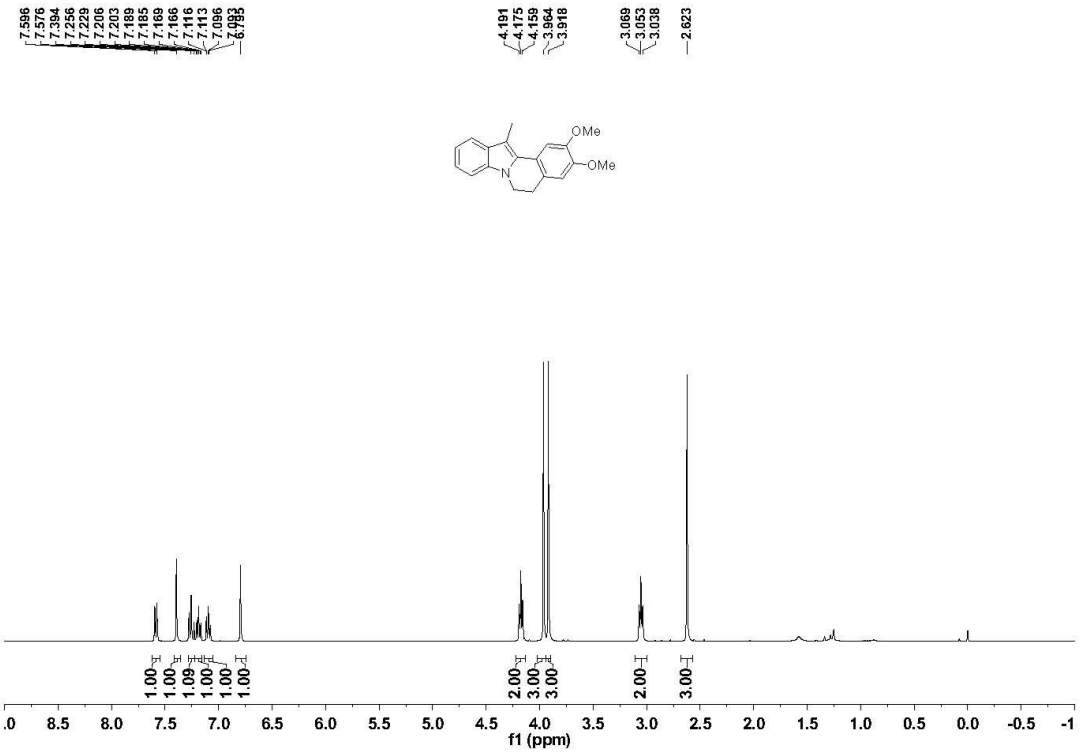

134.21
133.66
133.33
131.60
129.58
128.49
127.42
127.28
125.86
124.17
124.09
123.78
123.46
123.15
119.09
115.65
115.62
115.58
115.55
107.35
106.23
106.18
106.14
106.09
40.28
29.98
10.72
F3C
f1 (ppm)

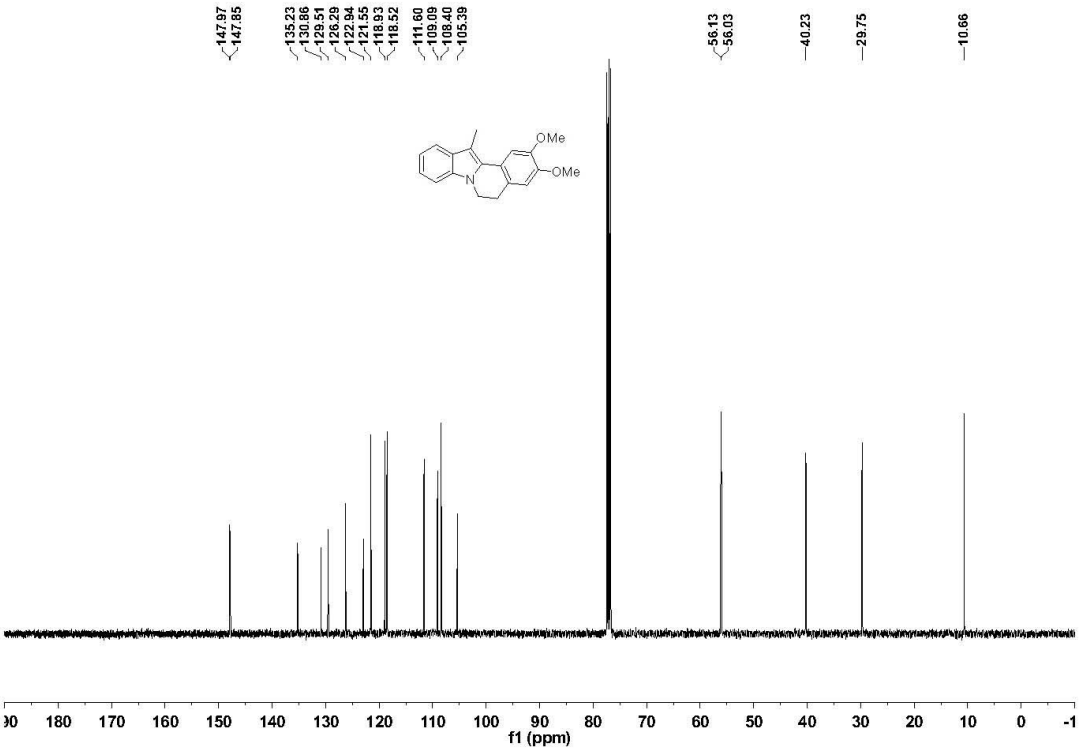
Compound 2c


7.787
7.785
7.594
7.591
7.589
7.574
7.571
7.569
7.276
7.274
7.272
7.256
7.254
7.252
7.199
7.196
7.181
7.178
7.175
7.161
7.158
7.113
7.110
7.096
7.093
7.090
6.909
6.902
6.888
6.881
6.833
6.827
4.192
4.177
4.161
3.836
3.101
3.085
3.069
2.588
OMe
1.00
1.00
1.00
1.00
1.01
0.99
1.00
2.00
3.00
2.00
3.00
f1 (ppm)

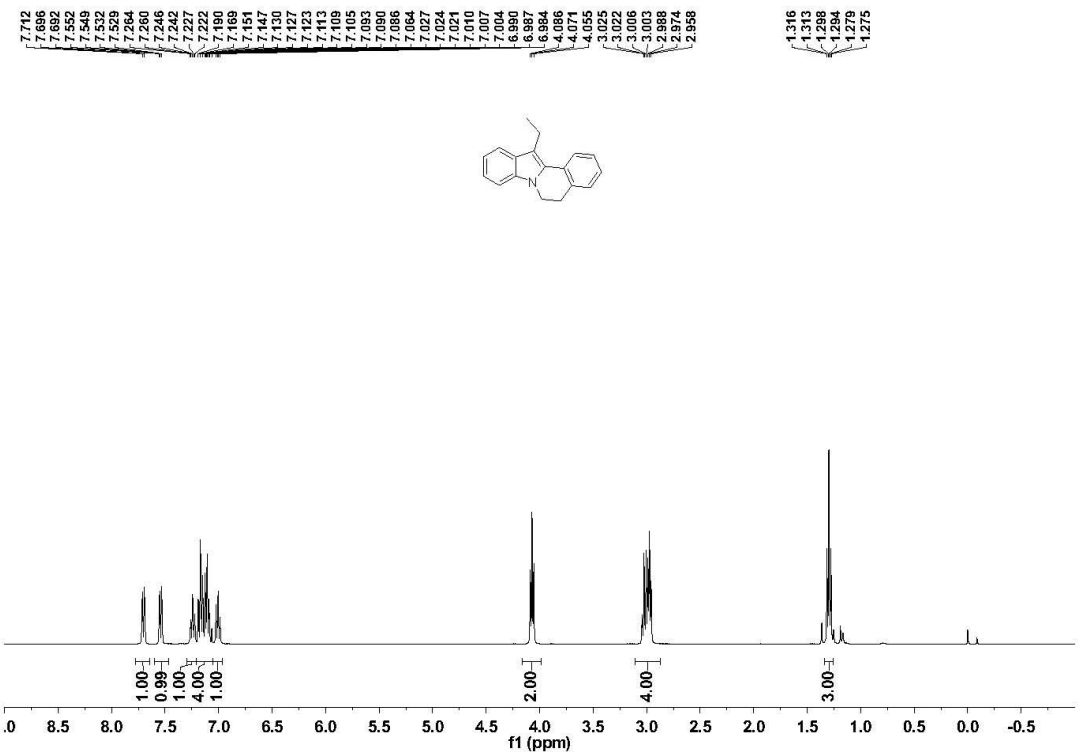

158.33
135.23
135.13
130.85
129.52
126.86
123.29
121.41
118.92
118.52
113.97
112.54
108.39
105.49
55.37
40.01
30.55
10.69
OMe
f1 (ppm)

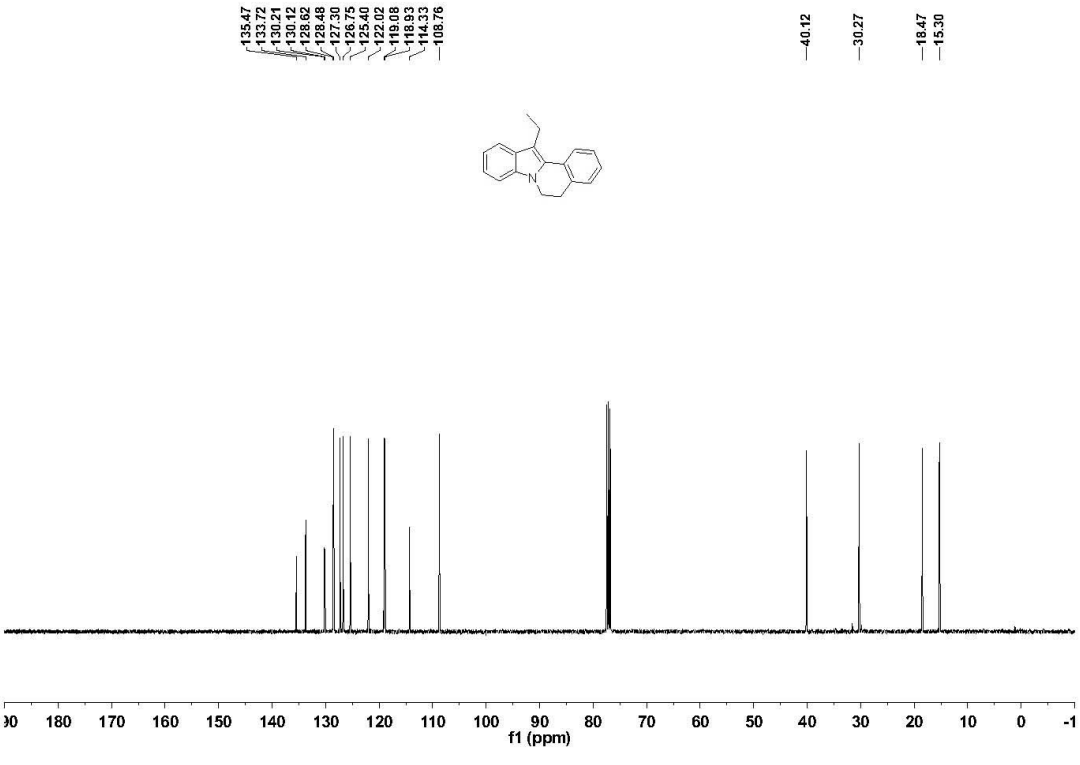
Compound 2d


7.596
7.576
7.394
7.256
7.229
7.206
7.203
7.189
7.185
7.169
7.166
7.116
7.113
7.096
7.093
6.793
4.191
4.175
4.159
3.964
3.918
3.069
3.053
3.038
2.623
OMe
OMe
1.00
1.00
1.09
1.00
1.00
2.00
3.00
3.00
2.00
3.00
f1 (ppm)

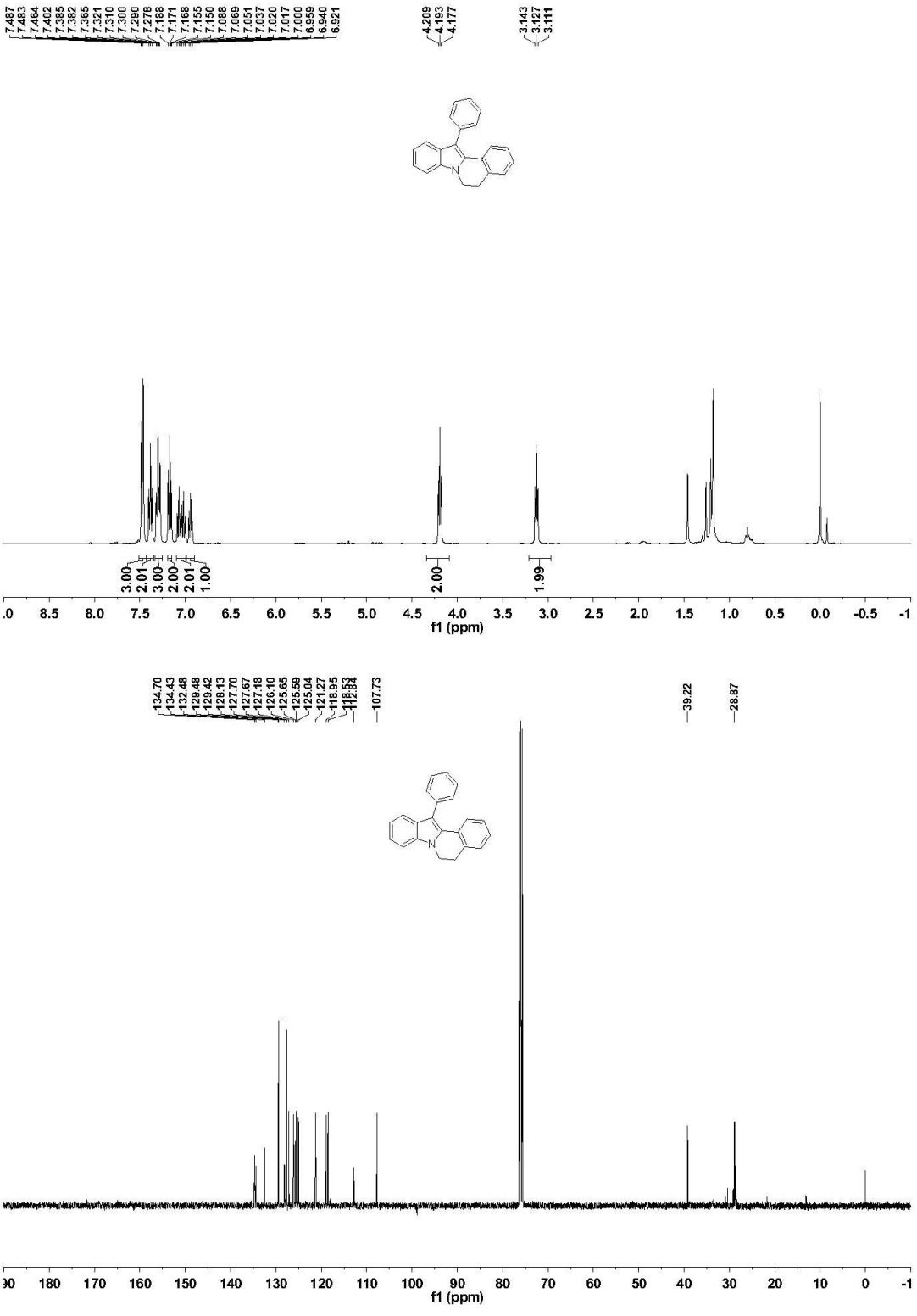

147.97
147.85
135.23
130.86
129.51
126.29
122.94
121.55
118.93
118.52
111.60
109.09
108.40
105.39
56.13
56.03
40.23
29.75
10.66
OMe
OMe
f1 (ppm)

Compound 2e

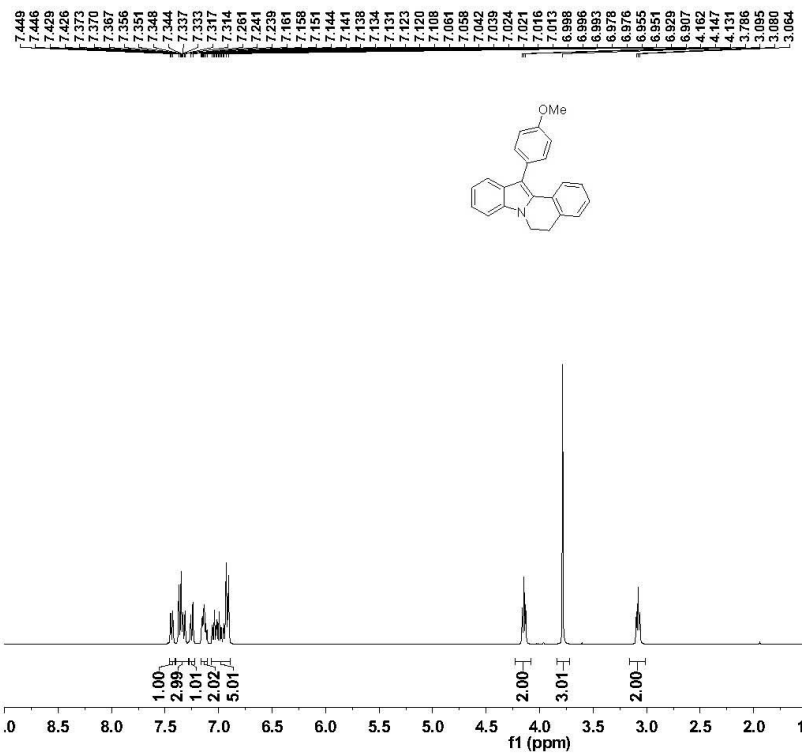

7.712
7.696
7.692
7.552
7.549
7.532
7.529
7.264
7.260
7.246
7.242
7.227
7.222
7.190
7.169
7.151
7.147
7.130
7.127
7.123
7.113
7.109
7.105
7.093
7.090
7.086
7.064
7.027
7.024
7.021
7.010
7.007
7.004
6.990
6.987
6.984
4.086
4.071
4.055
3.025
3.022
3.006
3.003
2.988
2.974
2.958
1.316
1.313
1.298
1.294
1.279
1.275
1.00
0.99
1.00
4.00
1.00
2.00
4.00
3.00
f1 (ppm)

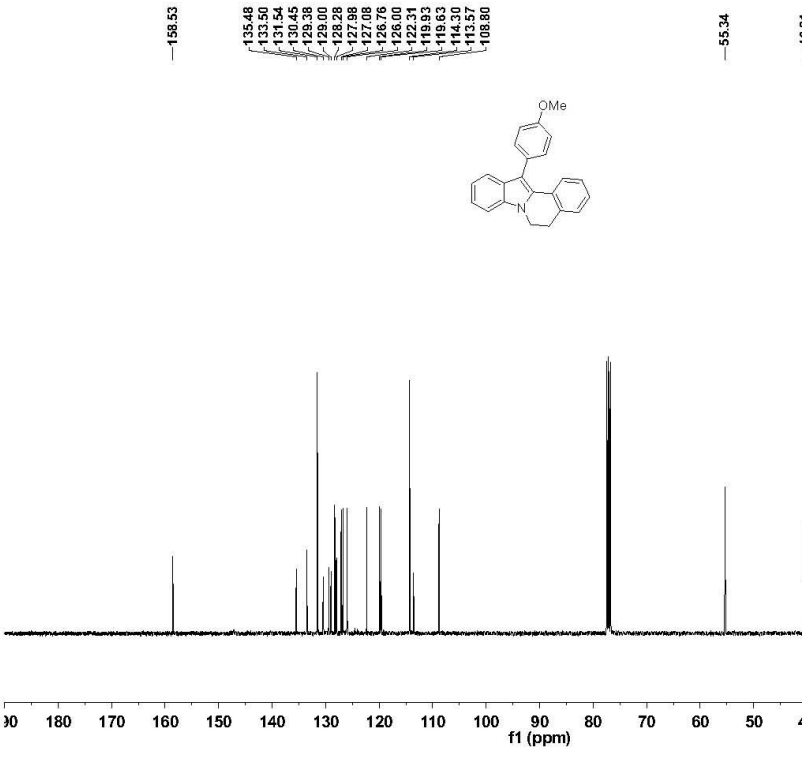

135.47
133.72
130.21
130.12
128.62
128.48
127.30
126.75
125.40
122.02
119.08
118.93
114.33
108.76
40.12
30.27
18.47
15.30
f1 (ppm)

Compound 2f

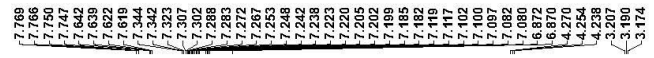

7.487
7.483
7.464
7.402
7.385
7.382
7.365
7.321
7.310
7.300
7.290
7.278
7.188
7.171
7.168
7.155
7.150
7.088
7.069
7.051
7.037
7.020
7.017
7.000
6.959
6.940
6.921
4.209
4.193
4.177
3.143
3.127
3.111
3.00
2.01
3.00
2.00
2.01
1.00
2.00
1.99
f1 (ppm)
134.70
134.43
132.48
129.48
129.42
128.13
127.70
127.67
127.18
126.10
125.65
125.59
125.04
121.27
118.95
107.73
39.22
28.87
f1 (ppm)

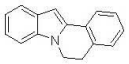
Compound 2g

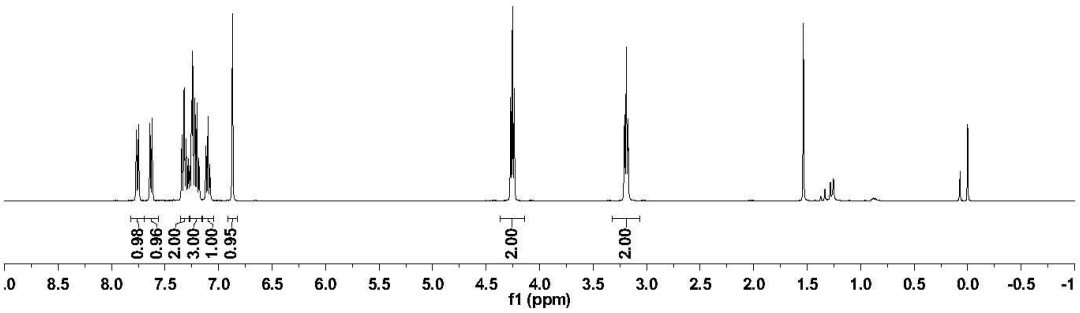

7.449
7.446
7.429
7.426
7.373
7.370
7.367
7.356
7.351
7.348
7.344
7.337
7.333
7.317
7.314
7.261
7.241
7.239
7.161
7.158
7.151
7.144
7.141
7.138
7.134
7.131
7.123
7.120
7.108
7.061
7.058
7.042
7.039
7.024
7.021
7.016
7.013
6.998
6.996
6.993
6.978
6.976
6.955
6.951
6.929
6.907
4.162
4.147
4.131
3.786
3.095
3.080
3.064
OMe
1.00
2.99
1.01
2.02
5.01
2.00
3.01
2.00
f1 (ppm)

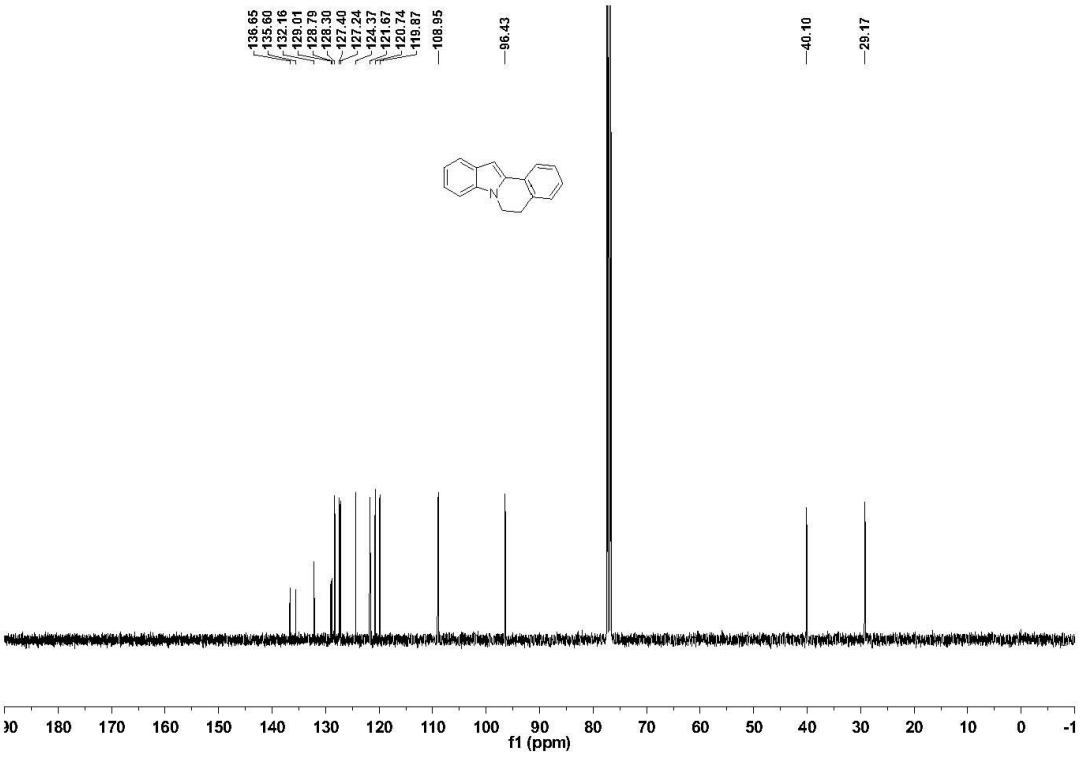

158.53
135.48
133.50
131.54
130.45
129.38
129.00
128.28
127.98
127.08
126.76
126.00
122.31
119.93
119.63
114.30
113.57
108.80
55.34
40.31
29.96
OMe
f1 (ppm)

Compound 2h

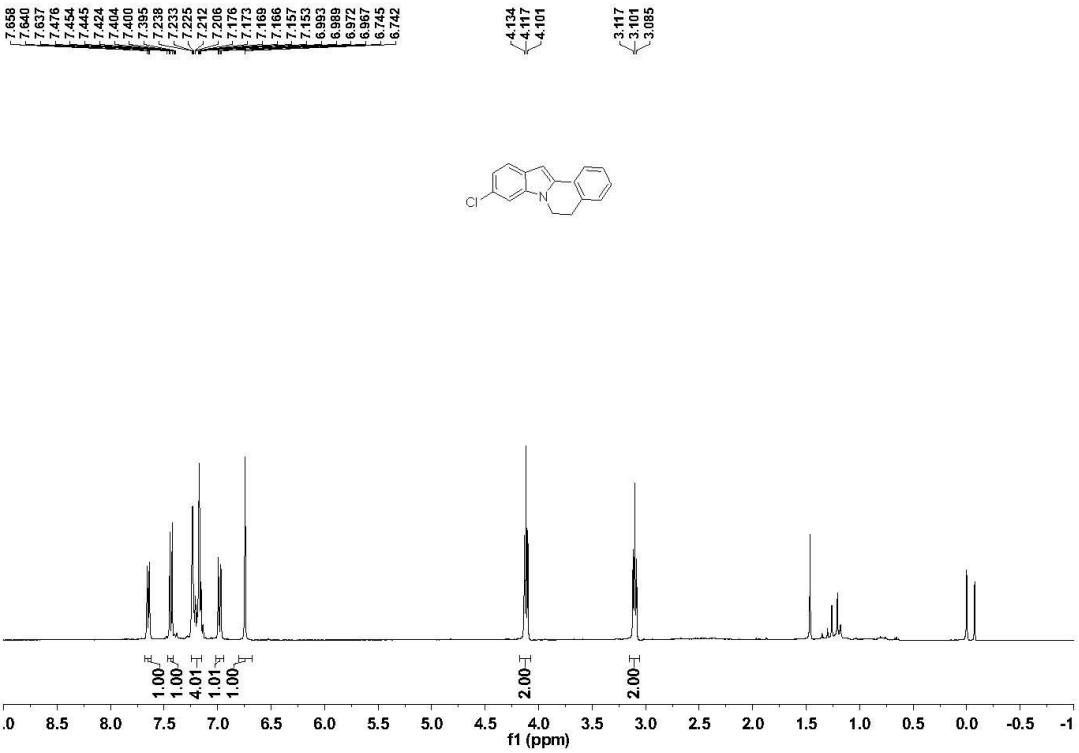

7.769
7.766
7.750
7.747
7.642
7.639
7.622
7.619
7.344
7.342
7.323
7.307
7.302
7.288
7.283
7.272
7.267
7.253
7.248
7.242
7.238
7.223
7.220
7.205
7.202
7.198
7.185
7.182
7.119
7.117
7.102
7.100
7.097
7.082
7.080
6.872
6.870
4.270
4.254
4.238
3.207
3.190
3.174

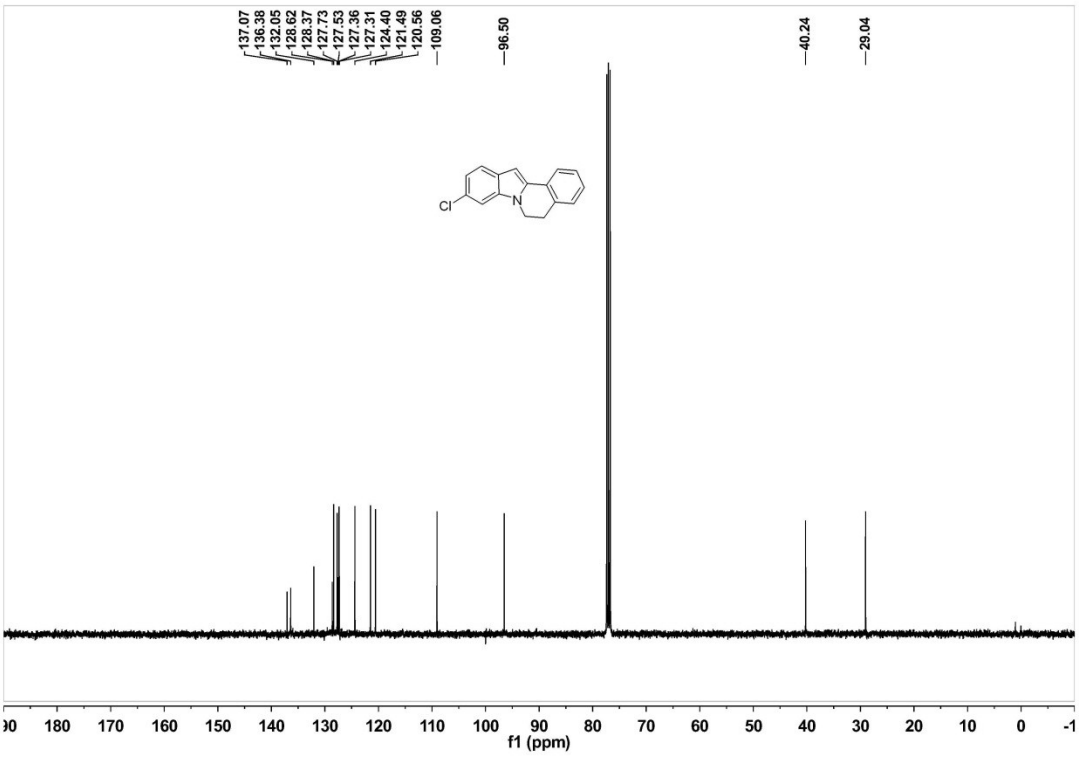



0.98
0.96
2.00
3.00
1.00
0.95
2.00
2.00
f1 (ppm)

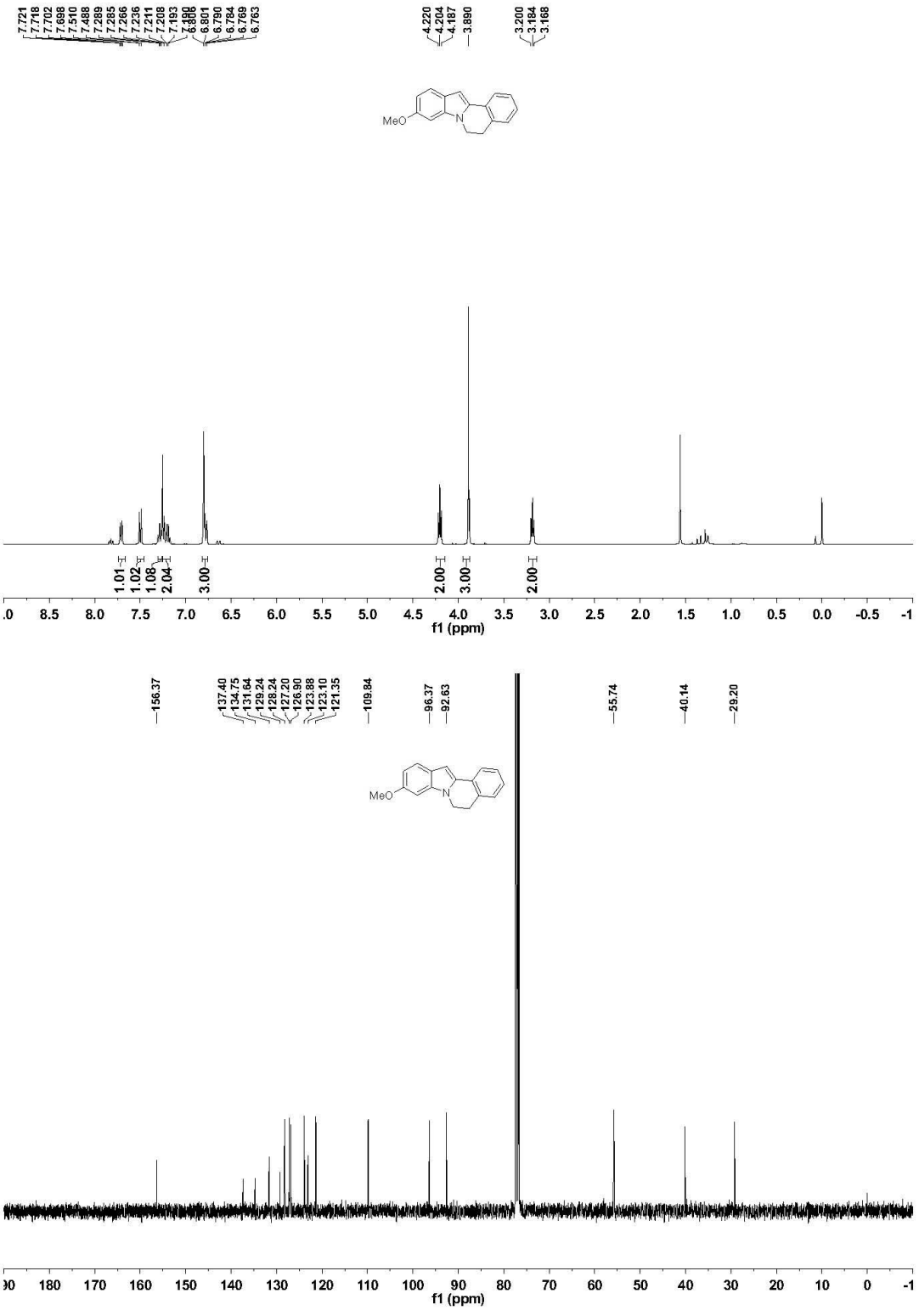

136.65
135.60
132.16
129.01
128.79
128.30
127.40
127.24
124.37
121.67
120.74
119.87
108.95
96.43
40.10
28.17
f1 (ppm)

Compound 2i

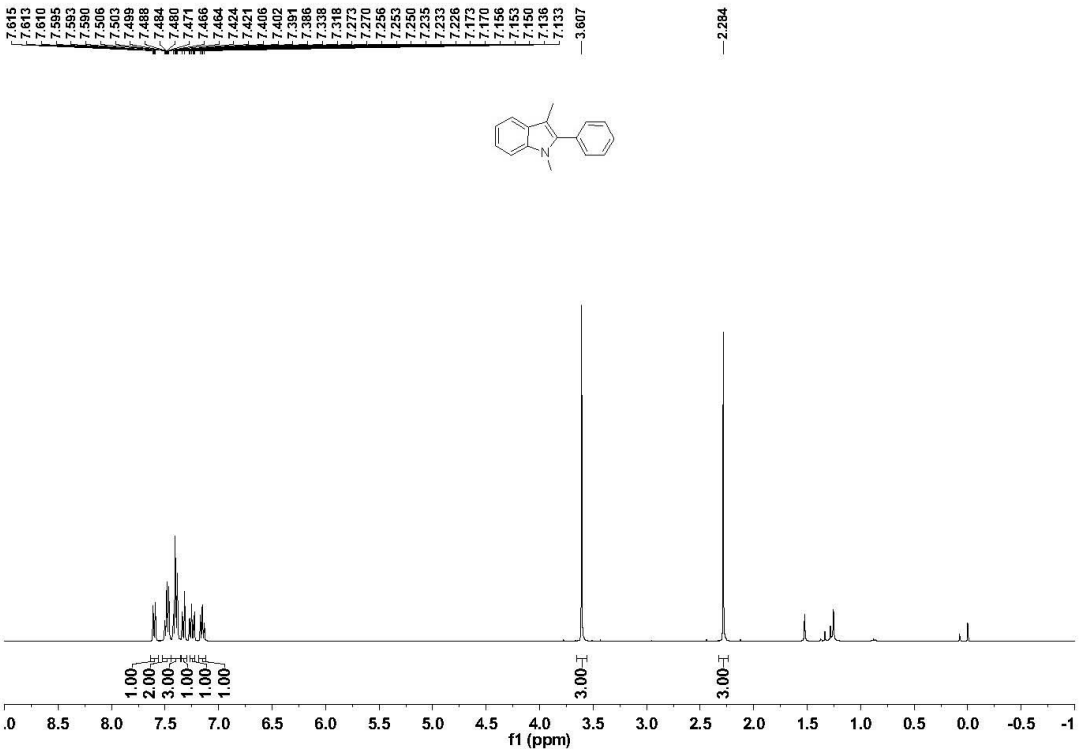

7.658
7.640
7.637
7.476
7.454
7.445
7.424
7.404
7.400
7.395
7.238
7.233
7.225
7.212
7.206
7.176
7.173
7.169
7.166
7.157
7.153
6.993
6.989
6.972
6.967
6.745
6.742
4.134
4.117
4.101
3.117
3.101
3.085
Cl
N
1.00
1.00
4.01
1.01
1.00
2.00
2.00
f1 (ppm)

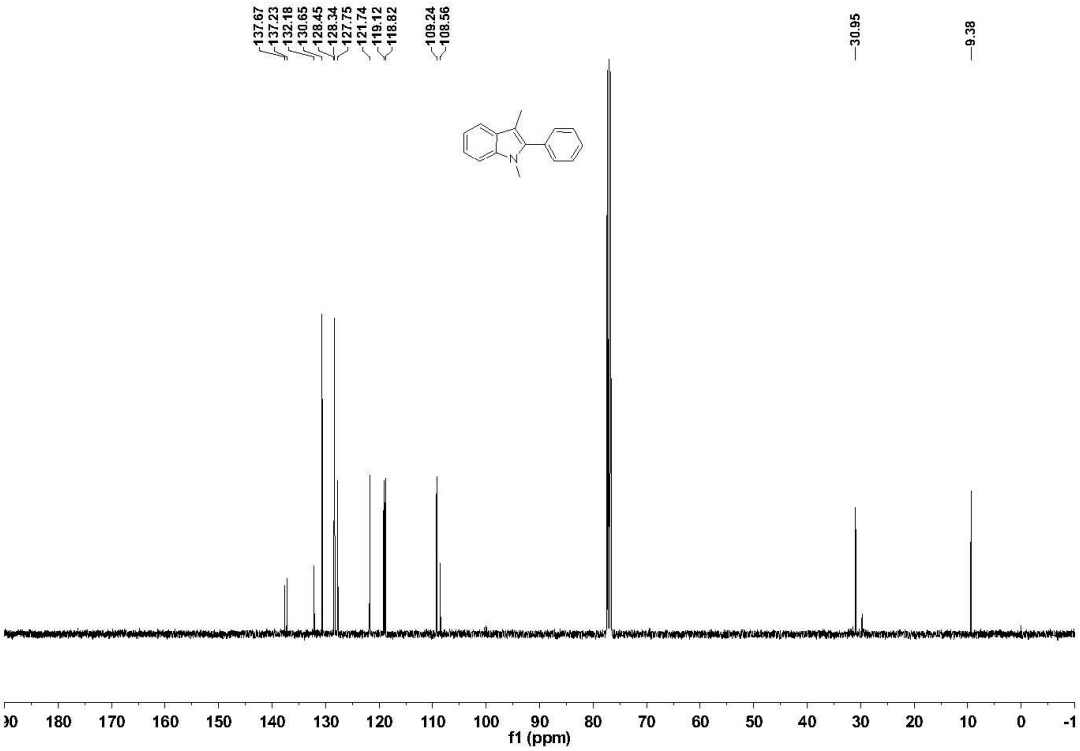

137.07
136.38
132.05
128.62
128.37
127.73
127.53
127.36
127.31
124.40
121.49
120.56
109.06
96.50
40.24
29.04
Cl
N
f1 (ppm)

Compound 2j

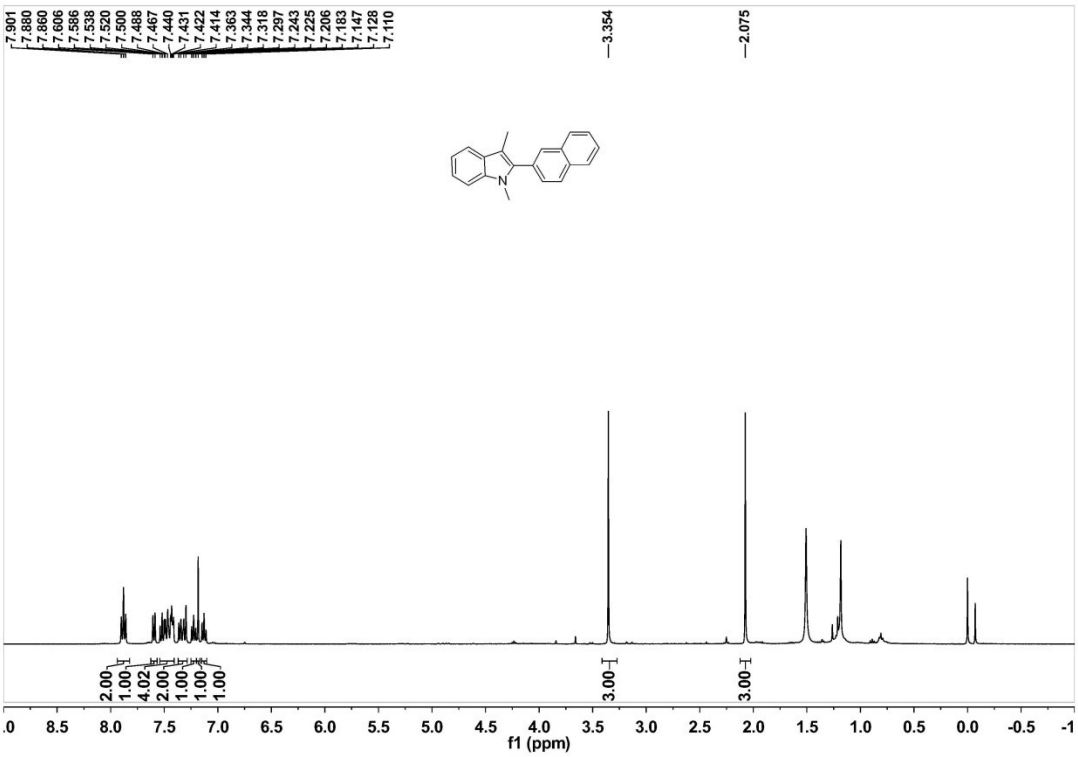

7.721
7.718
7.702
7.698
7.510
7.488
7.289
7.285
7.266
7.236
7.211
7.208
7.193
6.801
6.790
6.784
6.769
6.763
4.220
4.204
4.187
3.890
3.200
3.184
3.168
MeO
1.01
1.02
1.08
2.04
3.00
2.00
3.00
2.00
f1 (ppm)
156.37
137.40
134.75
131.64
129.24
128.24
127.20
126.90
123.88
123.10
121.35
109.84
96.37
92.63
55.74
40.14
29.20
MeO
f1 (ppm)

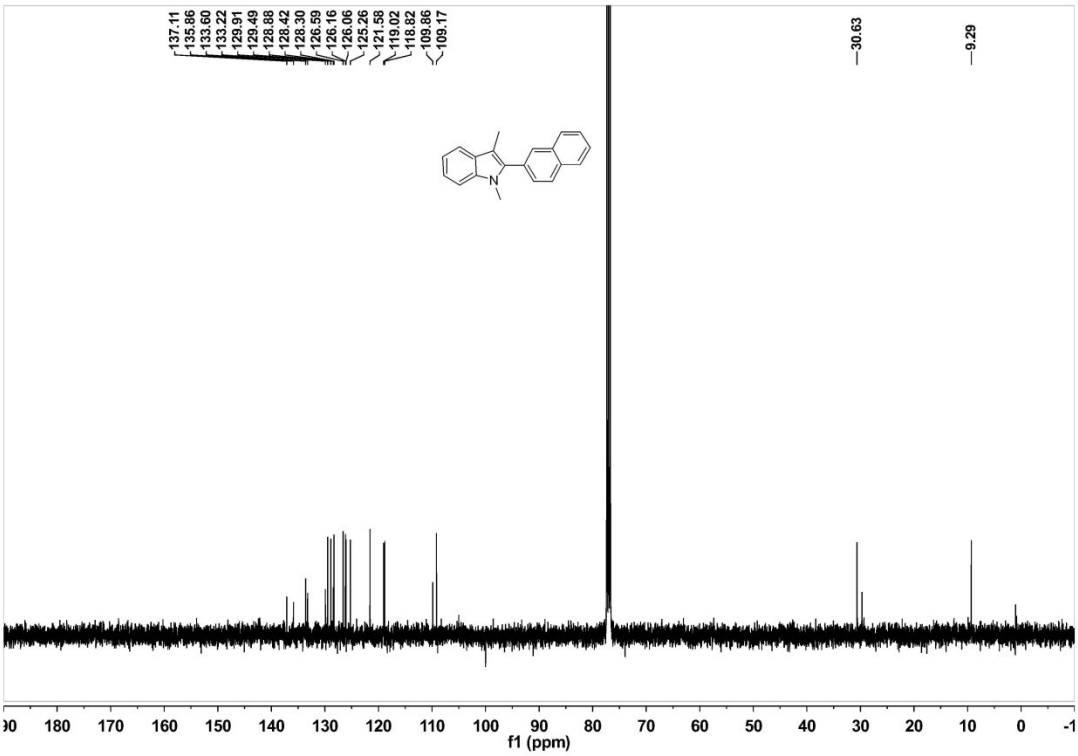
Compound 2k


7.615
7.613
7.610
7.595
7.593
7.590
7.506
7.503
7.499
7.488
7.484
7.480
7.471
7.466
7.464
7.424
7.421
7.406
7.402
7.391
7.386
7.338
7.318
7.273
7.270
7.256
7.253
7.250
7.235
7.233
7.226
7.173
7.170
7.156
7.153
7.150
7.136
7.133
3.607
2.284
1.00
2.00
3.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

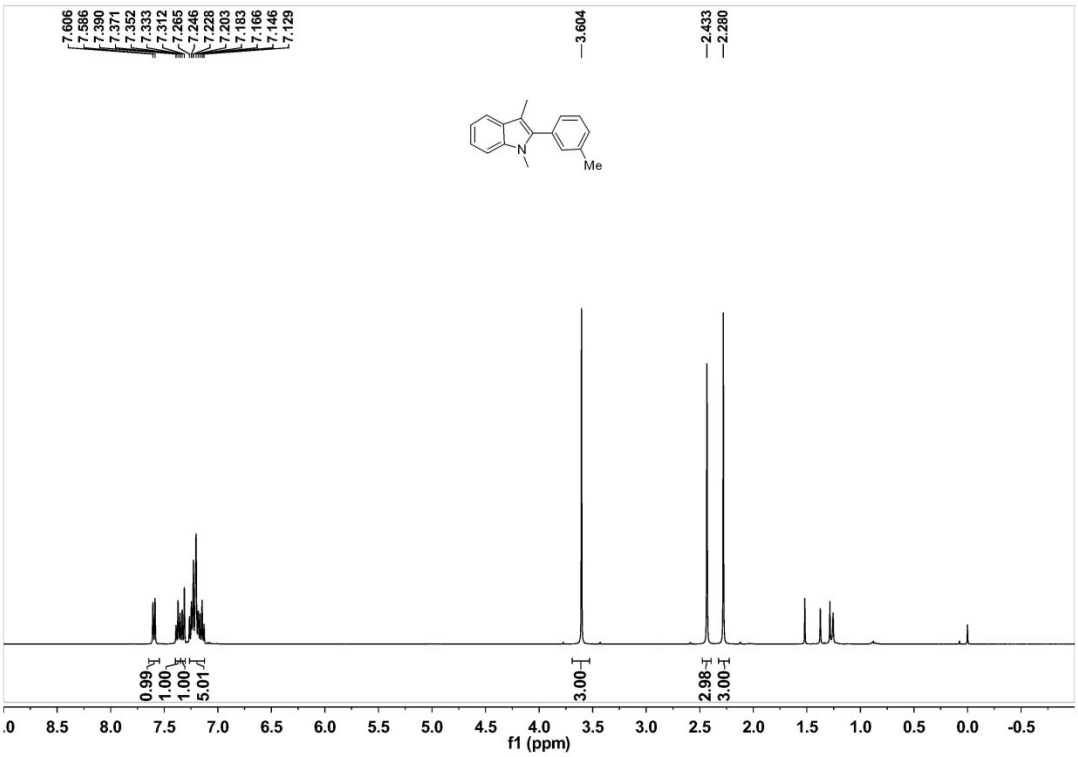

137.67
137.23
132.18
130.65
128.45
128.34
127.75
121.74
119.12
118.82
109.24
108.56
30.95
9.38
f1 (ppm)

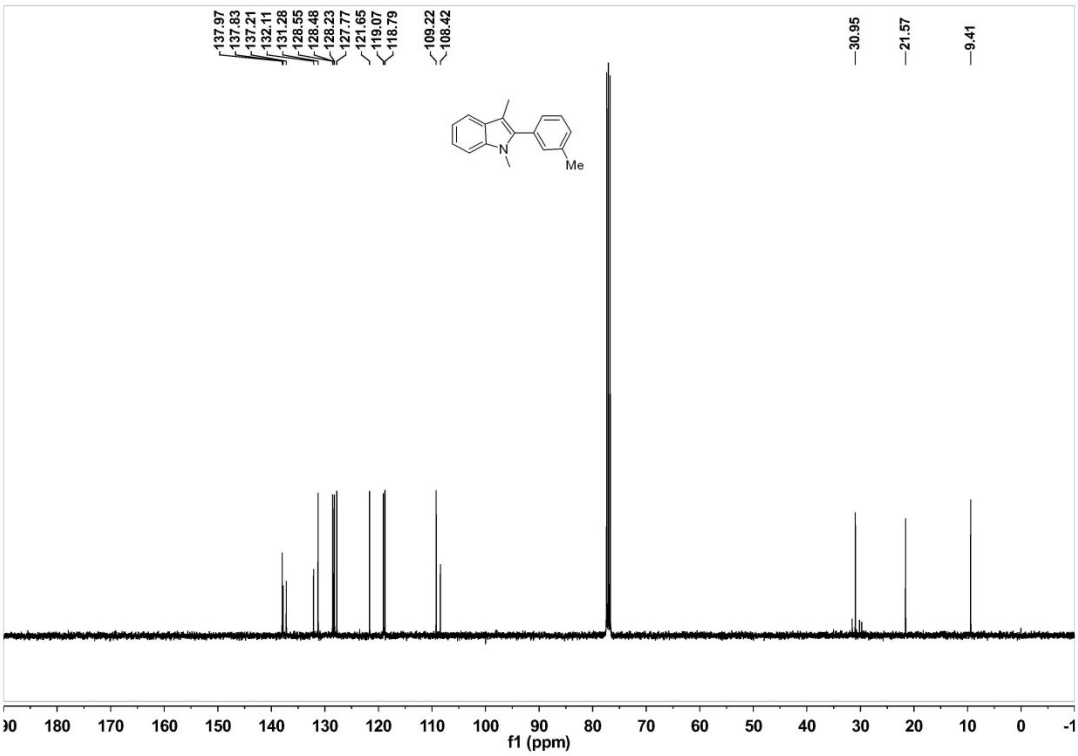
Compound 2l


7.901
7.880
7.860
7.606
7.586
7.538
7.520
7.500
7.488
7.467
7.440
7.431
7.422
7.414
7.363
7.344
7.318
7.297
7.243
7.225
7.206
7.183
7.147
7.128
7.110
3.354
2.075
2.00
1.00
4.02
2.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

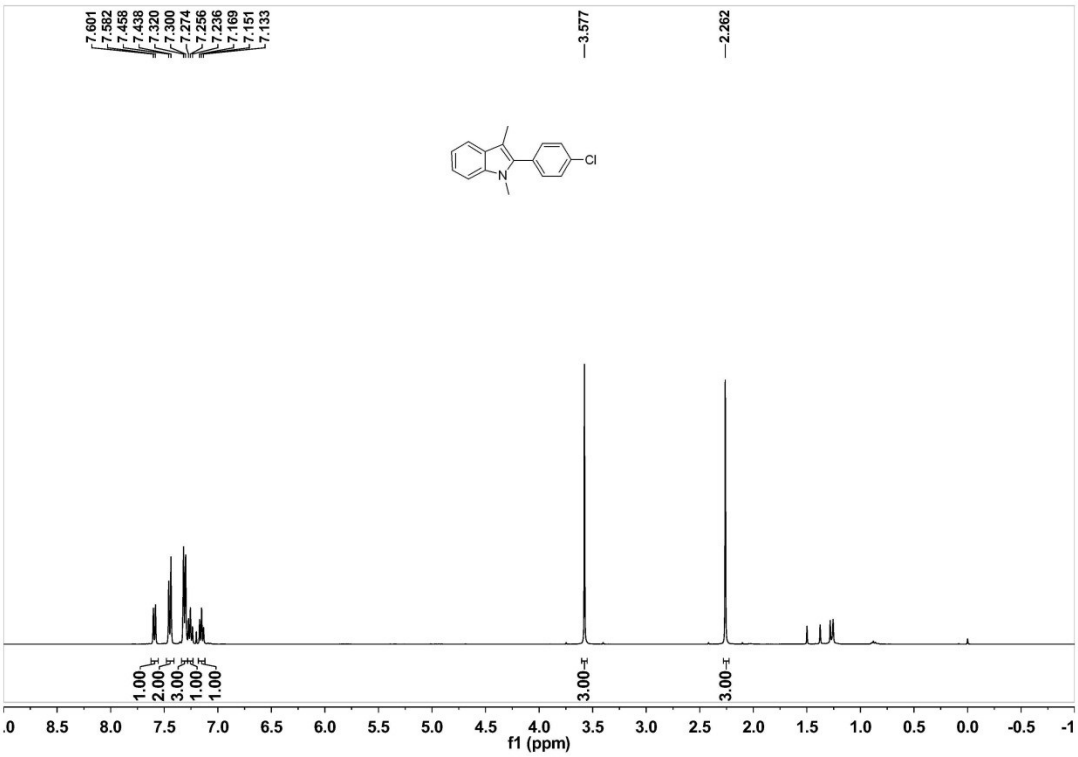

137.11
135.86
133.60
133.22
129.91
129.49
128.88
128.42
128.30
126.59
126.16
126.06
125.26
121.58
119.02
118.82
109.86
109.17
30.63
9.29
f1 (ppm)

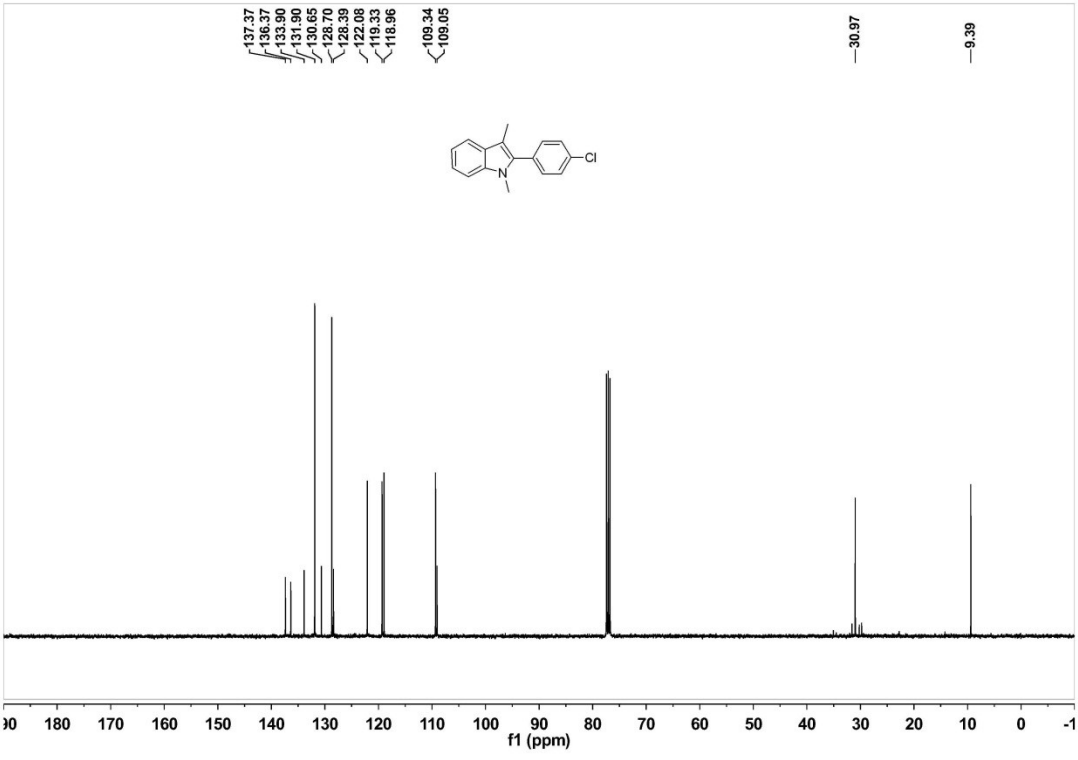
Compound 2m


7.606
7.586
7.390
7.371
7.352
7.333
7.312
7.265
7.246
7.228
7.203
7.183
7.166
7.146
7.129
3.604
2.433
2.280
Me
0.99
1.00
1.00
5.01
3.00
2.98
3.00
f1 (ppm)

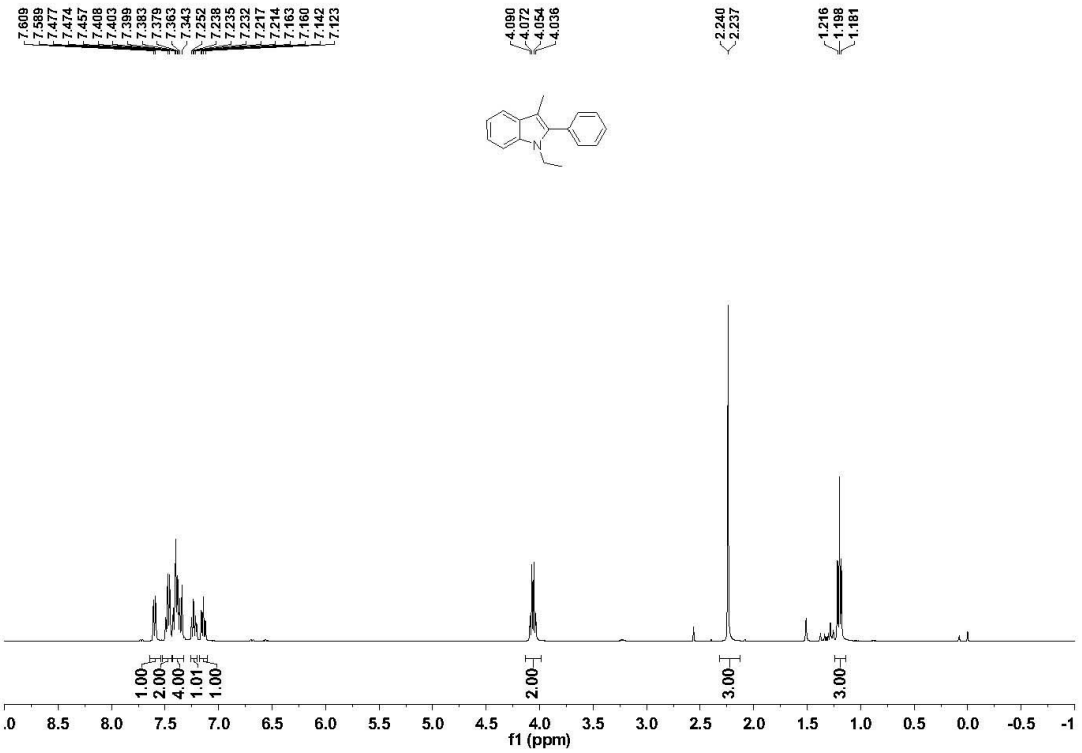

137.97
137.83
137.21
132.11
131.28
128.55
128.48
128.23
127.77
121.65
119.07
118.79
109.22
108.42
30.95
21.57
9.41
Me
f1 (ppm)

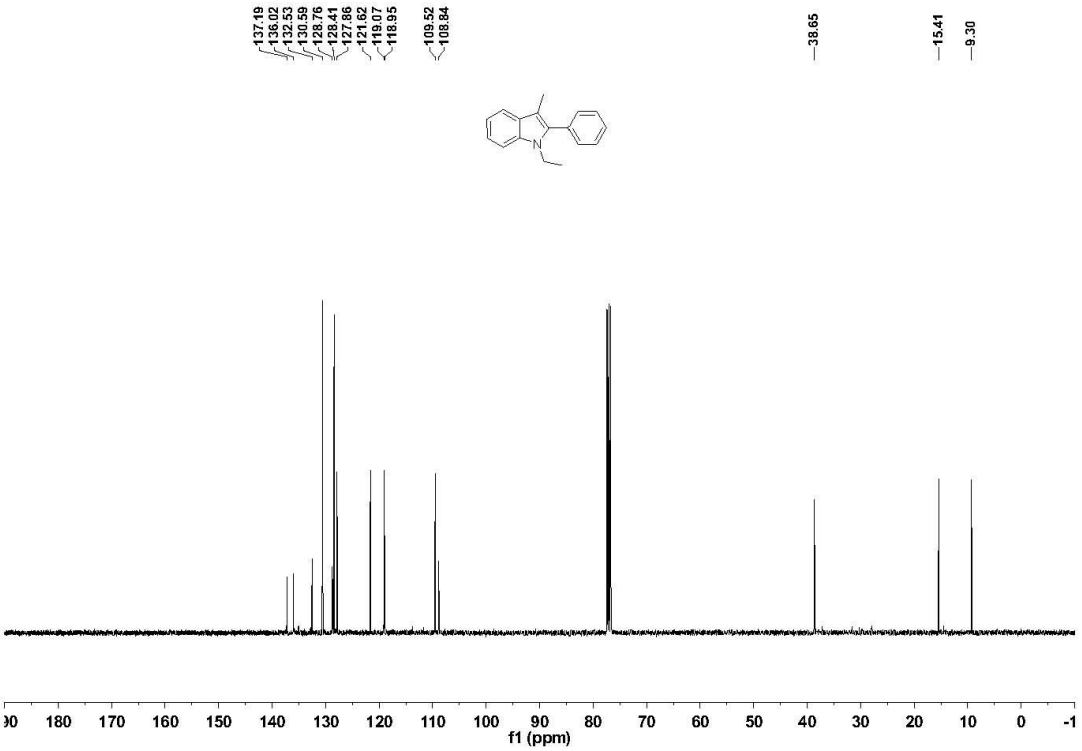
Compound 2n


7.601
7.582
7.458
7.438
7.320
7.300
7.274
7.256
7.236
7.169
7.151
7.133
3.577
2.262
Cl
N
1.00
2.00
3.00
1.00
1.00
3.00
3.00
f1 (ppm)

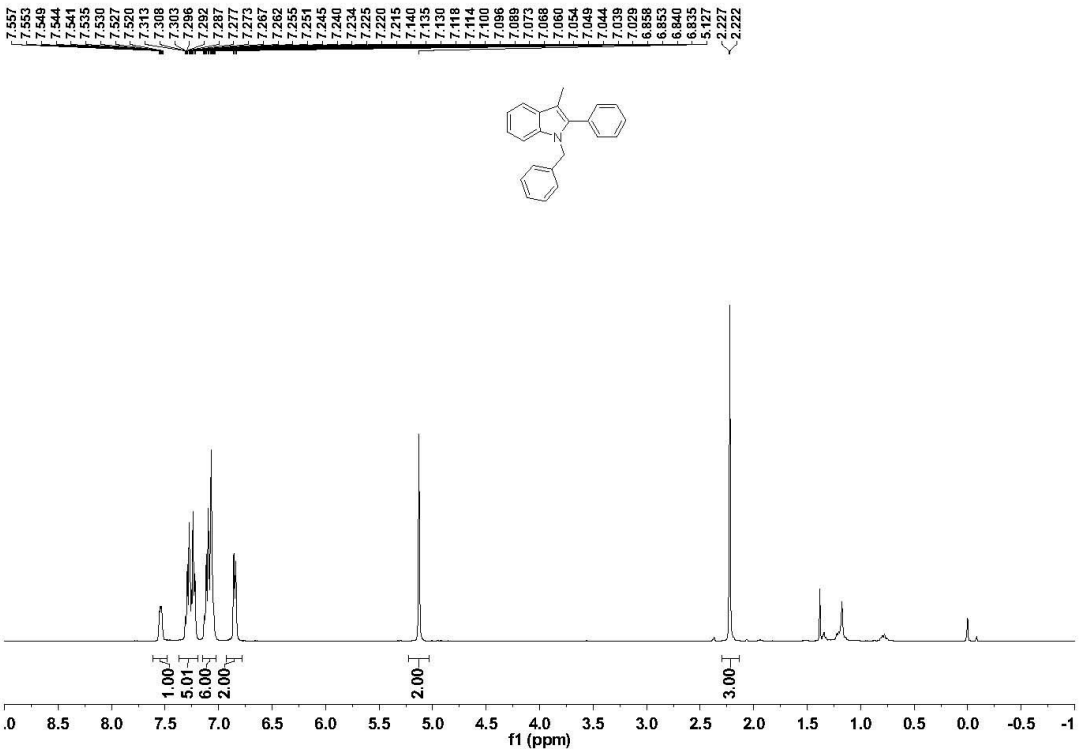

137.37
136.37
133.90
131.90
130.65
128.70
128.39
122.08
119.33
118.96
109.34
109.05
30.97
9.39
Cl
N
f1 (ppm)

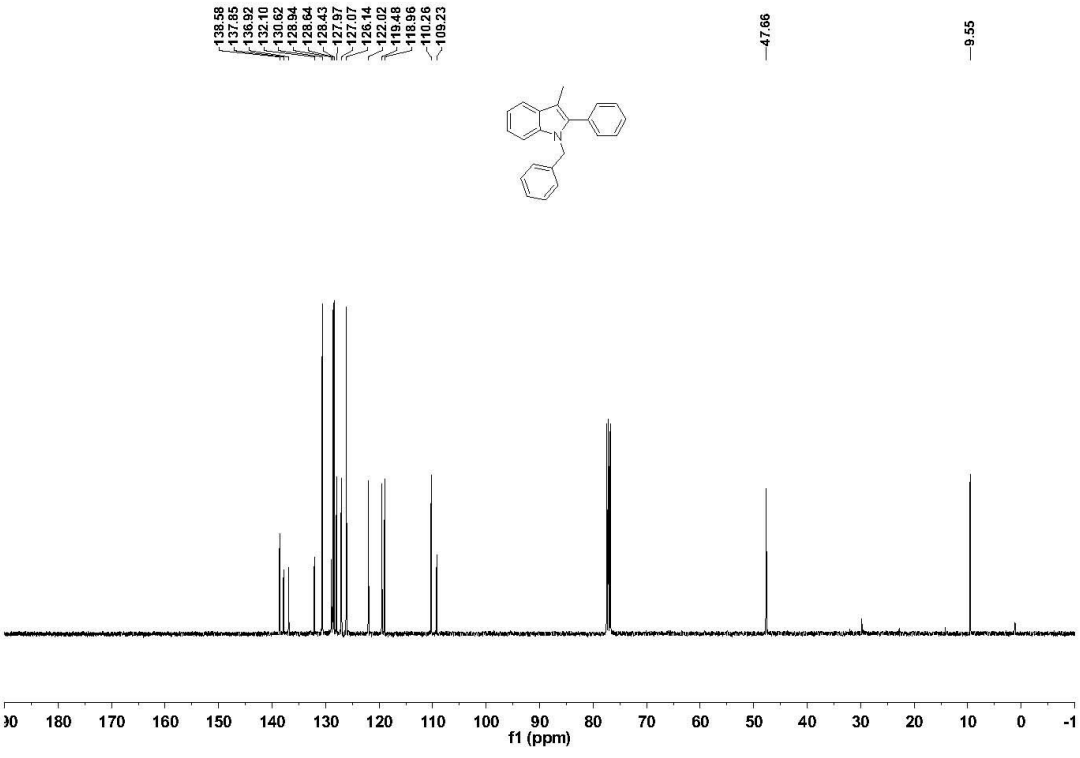
Compound 2o


7.609
7.589
7.477
7.474
7.457
7.408
7.403
7.399
7.383
7.379
7.363
7.343
7.252
7.238
7.235
7.232
7.217
7.214
7.163
7.160
7.142
7.123
4.090
4.072
4.054
4.036
2.240
2.237
1.216
1.198
1.181
1.00
2.00
4.00
1.01
1.00
2.00
3.00
3.00
f1 (ppm)

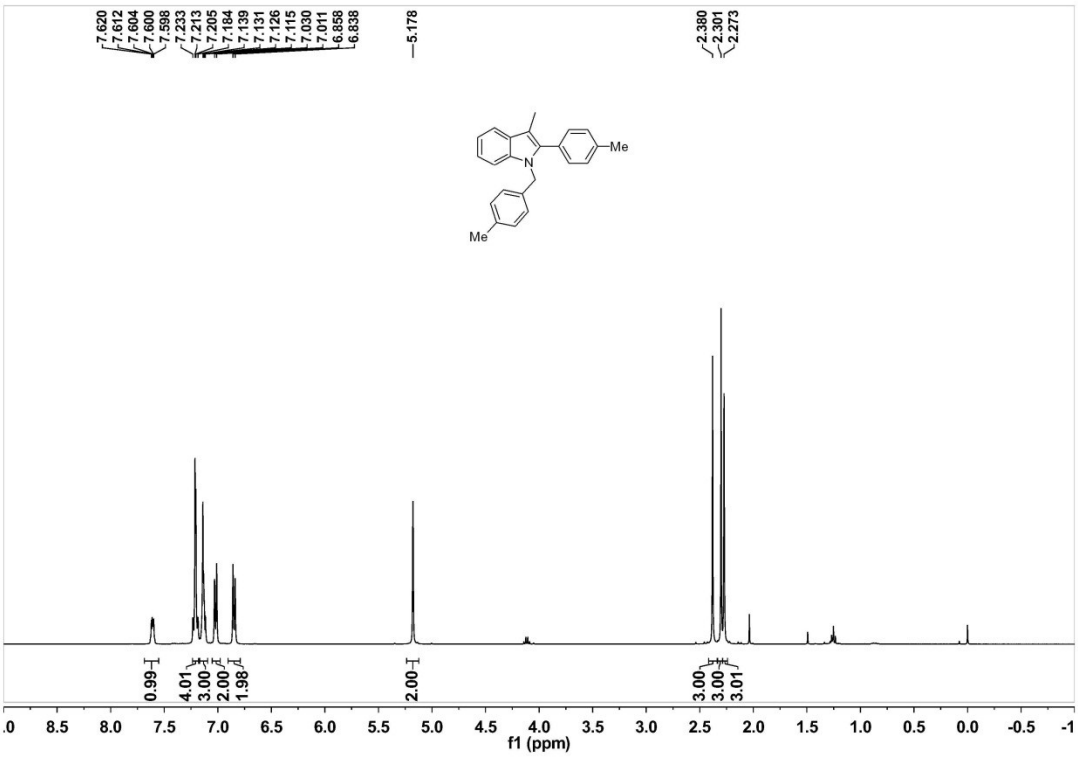

137.19
136.02
132.53
130.59
128.76
128.41
127.86
121.62
119.07
118.95
109.52
108.84
38.65
15.41
9.30
f1 (ppm)

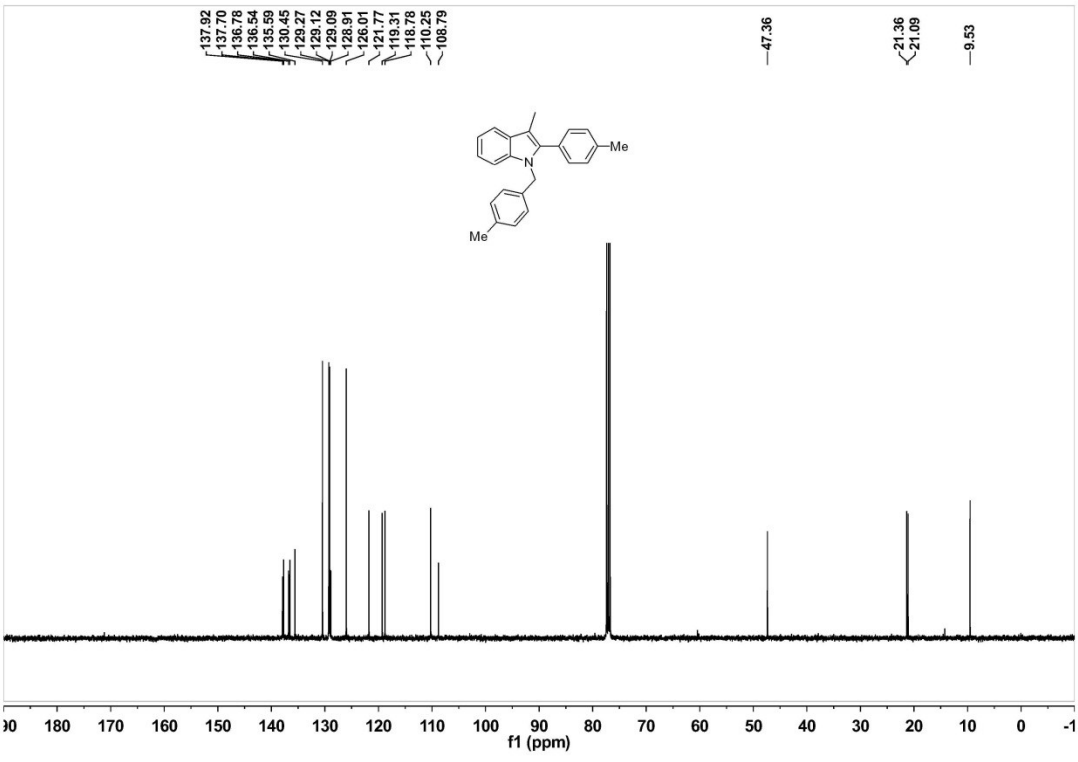
Compound 2p


7.557
7.553
7.549
7.544
7.541
7.535
7.530
7.527
7.520
7.313
7.308
7.303
7.296
7.292
7.287
7.277
7.273
7.267
7.262
7.255
7.251
7.245
7.240
7.234
7.225
7.220
7.215
7.140
7.135
7.130
7.118
7.114
7.100
7.096
7.089
7.073
7.068
7.060
7.054
7.049
7.044
7.039
7.029
6.858
6.853
6.840
6.835
5.127
2.227
2.222
1.00
5.01
6.00
2.00
2.00
3.00
f1 (ppm)

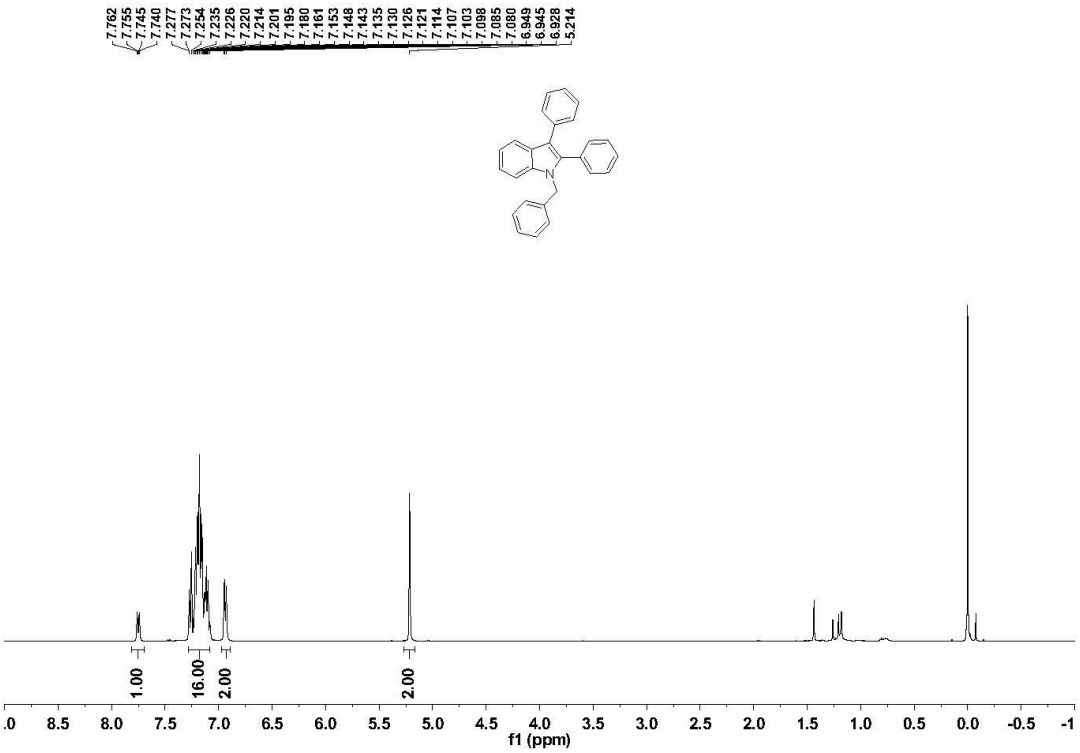

138.58
137.85
136.92
132.10
130.62
128.94
128.64
128.43
127.97
127.07
126.14
122.02
119.48
118.96
110.26
109.23
47.66
9.55
f1 (ppm)

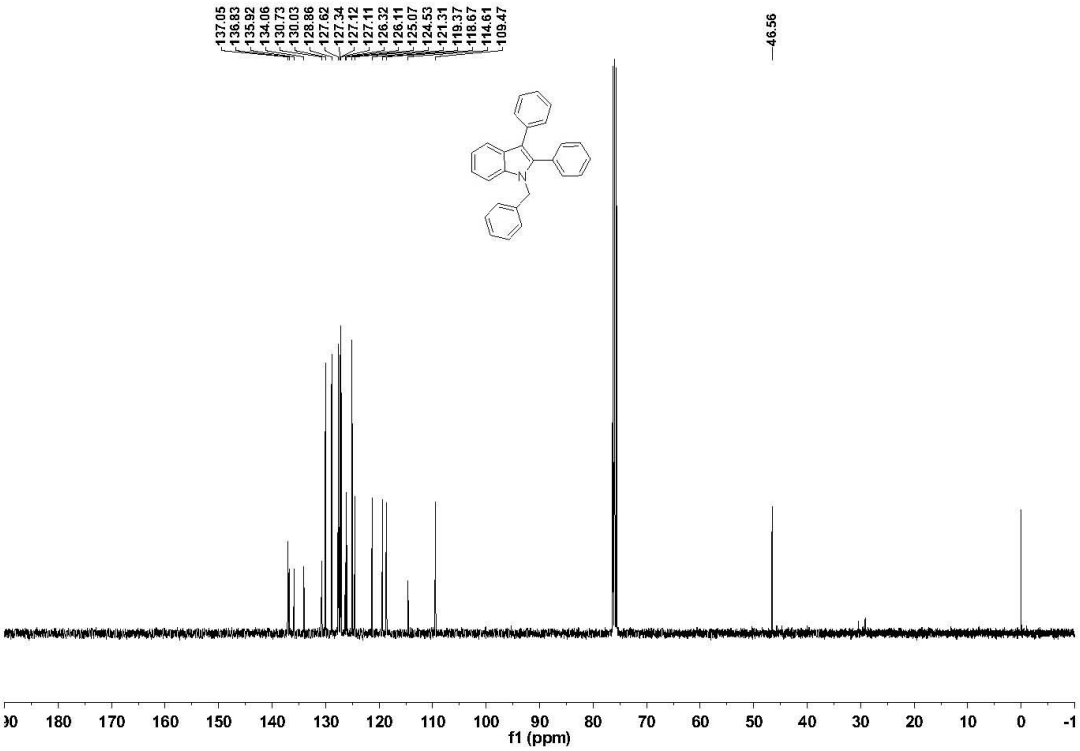
Compound 2q


7.620
7.612
7.604
7.600
7.598
7.233
7.213
7.205
7.184
7.139
7.131
7.126
7.115
7.030
7.011
6.858
6.838
5.178
2.380
2.301
2.273
Me
Me
0.99
4.01
3.00
2.00
1.98
2.00
3.00
3.00
3.01
f1 (ppm)

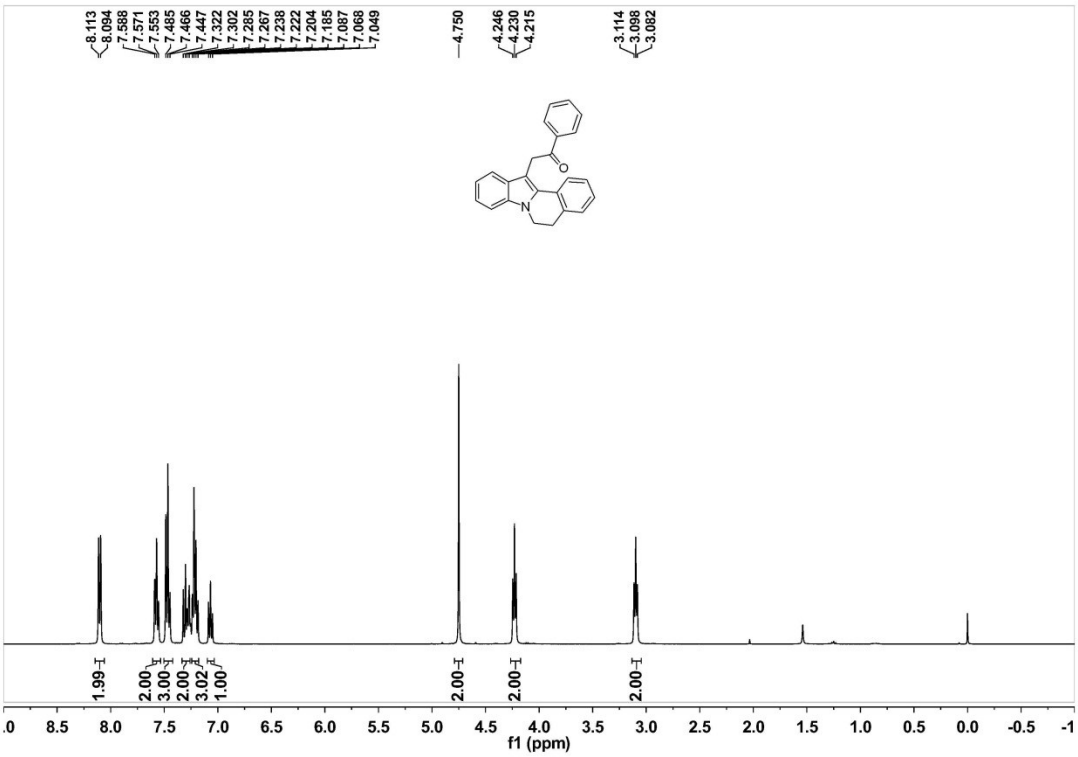

137.92
137.70
136.78
136.54
135.59
130.45
129.27
129.12
129.09
128.91
126.01
121.77
119.31
118.78
110.25
108.79
47.36
21.36
21.09
9.53
Me
Me
f1 (ppm)

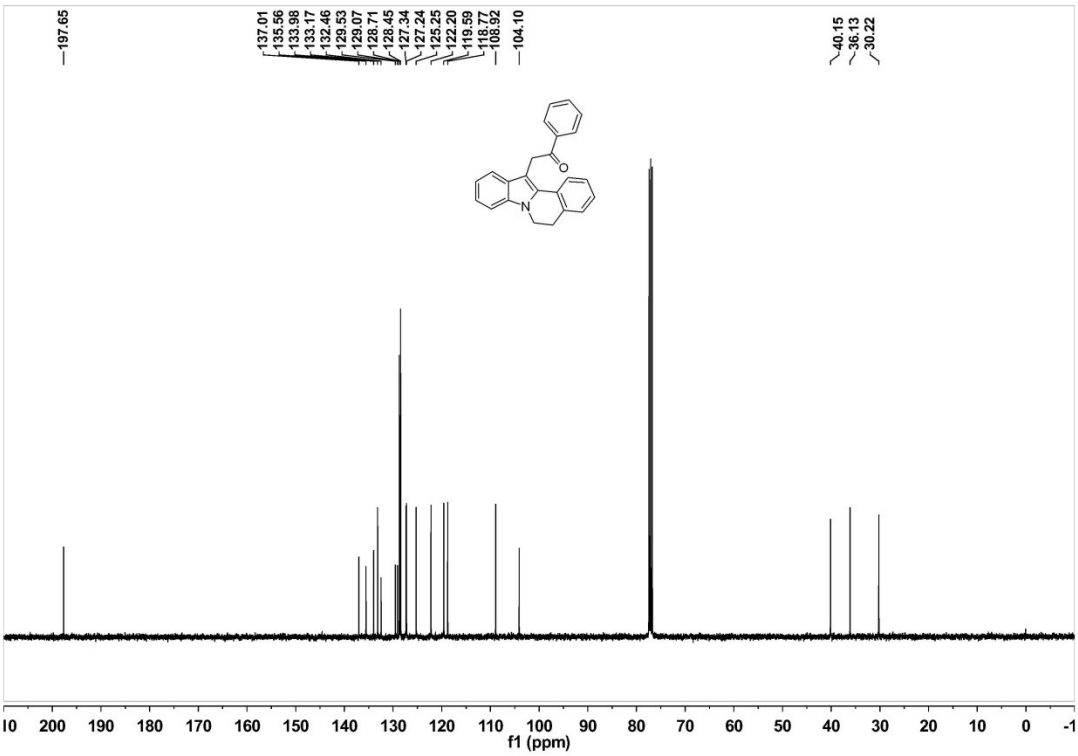
Compound 2r


7.762
7.755
7.745
7.740
7.277
7.273
7.254
7.235
7.226
7.220
7.214
7.201
7.195
7.180
7.161
7.153
7.148
7.143
7.135
7.130
7.126
7.121
7.114
7.107
7.103
7.098
7.085
7.080
6.949
6.945
6.928
5.214
1.00
16.00
2.00
2.00
f1 (ppm)

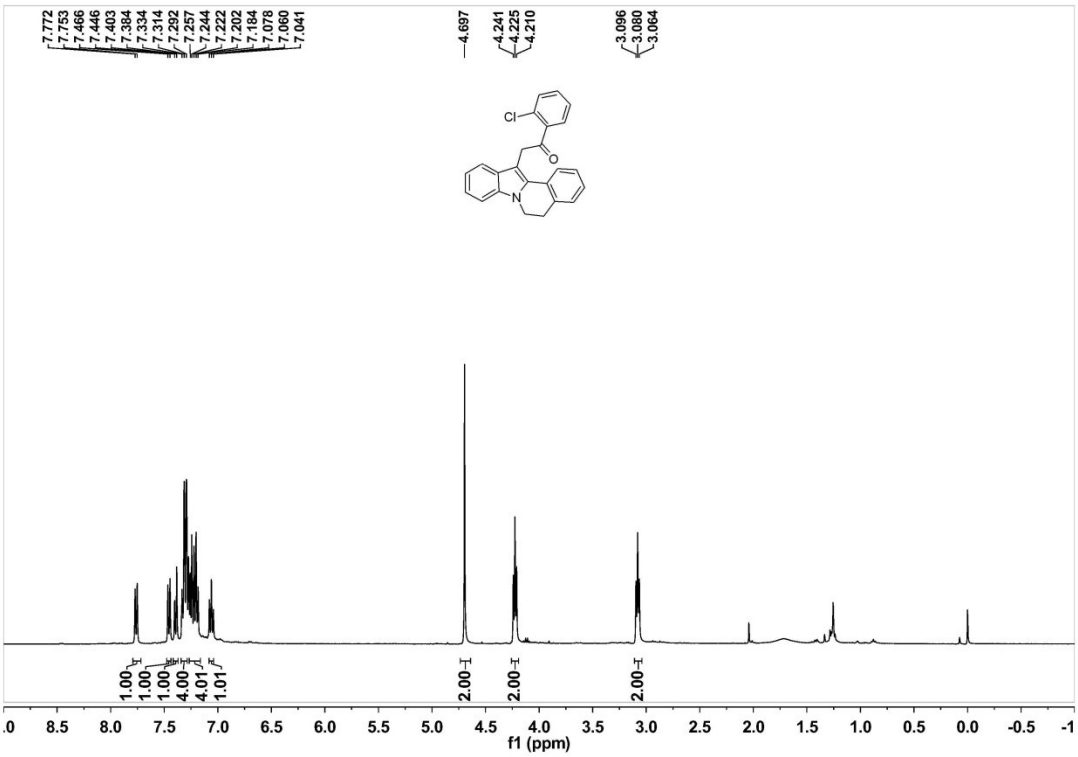

137.05
136.83
135.92
134.06
130.73
130.03
128.86
127.62
127.34
127.12
127.11
126.32
126.11
125.07
124.53
121.31
119.37
118.67
114.61
109.47
46.56
f1 (ppm)

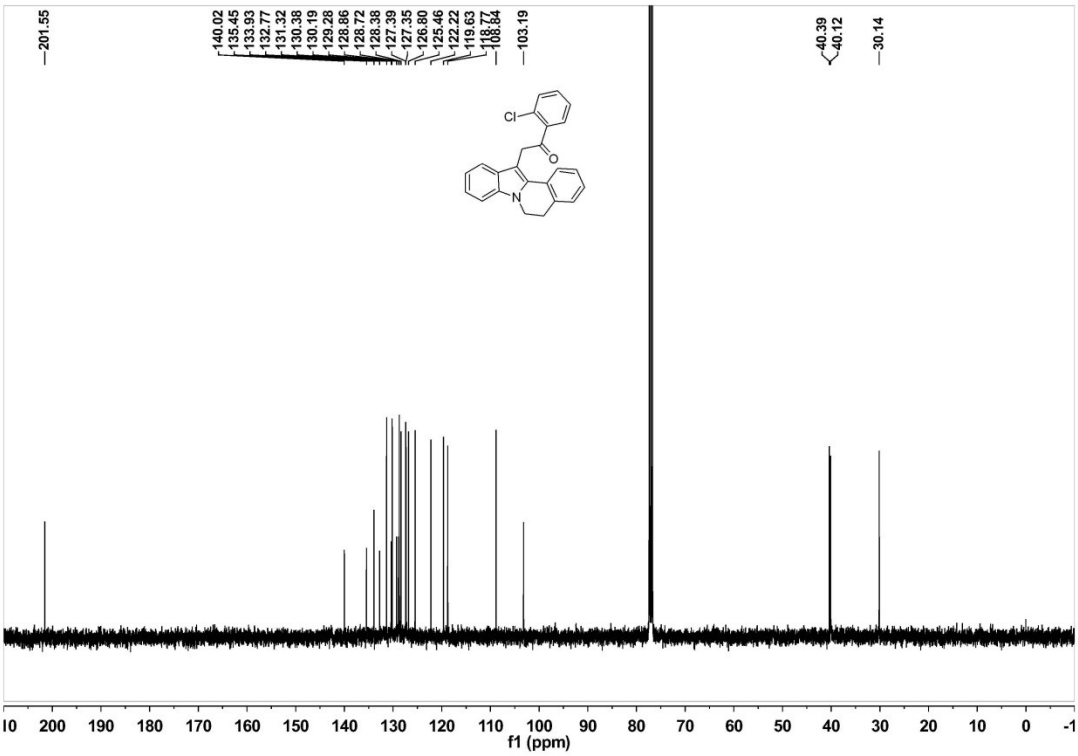
Compound 4a


8.113
8.094
7.588
7.571
7.553
7.485
7.466
7.447
7.322
7.302
7.285
7.267
7.238
7.222
7.204
7.185
7.087
7.068
7.049
4.750
4.246
4.230
4.215
3.114
3.098
3.082
1.99
2.00
3.00
2.00
3.02
1.00
2.00
2.00
2.00
f1 (ppm)

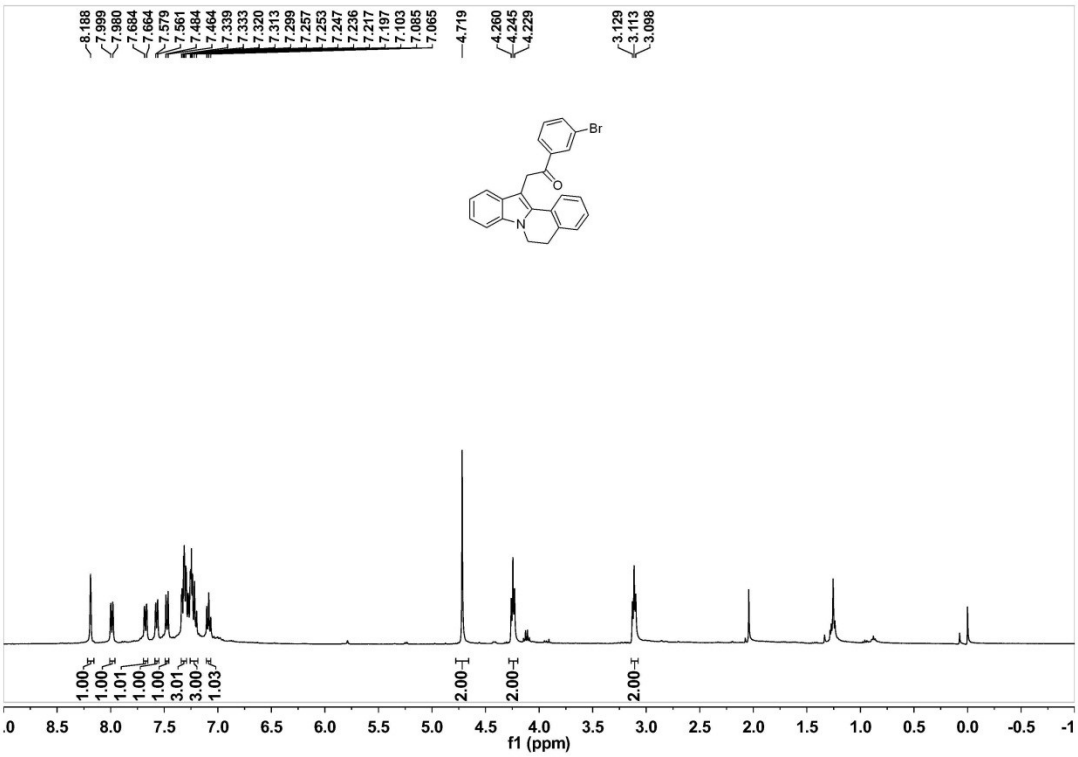

197.65
137.01
135.56
133.98
133.17
132.46
129.53
129.07
128.71
128.45
127.34
127.24
125.25
122.20
119.59
118.77
108.92
104.10
40.15
36.13
30.22
f1 (ppm)

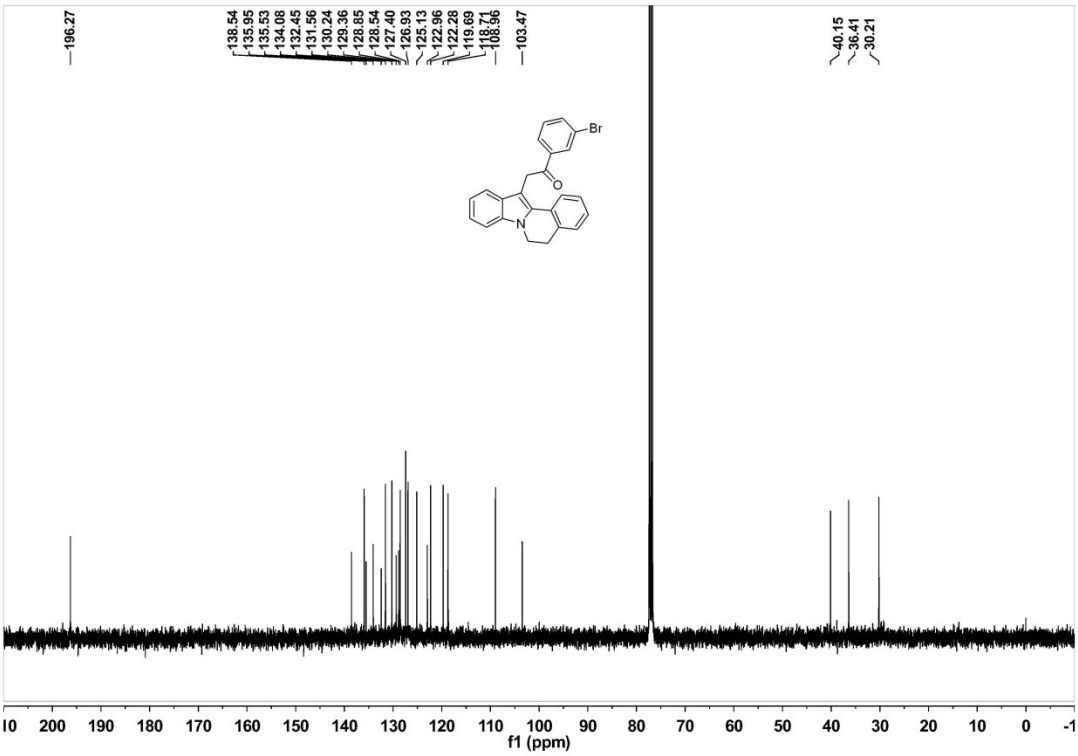
Compound 4b


7.772
7.753
7.466
7.446
7.403
7.384
7.334
7.314
7.292
7.257
7.244
7.222
7.202
7.184
7.078
7.060
7.041
4.697
4.241
4.225
4.210
3.096
3.080
3.064
Cl
O
N
1.00
1.00
1.00
4.00
4.01
1.01
2.00
2.00
2.00
f1 (ppm)

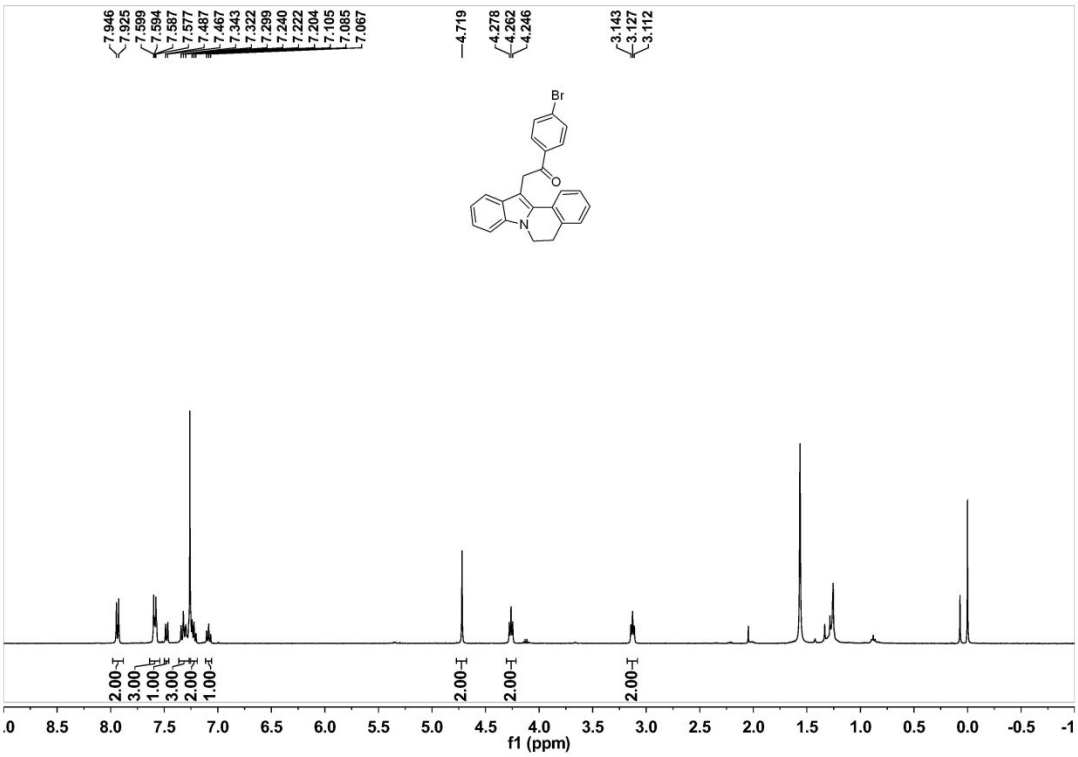

201.55
140.02
135.45
133.93
132.77
131.32
130.38
130.19
129.28
128.86
128.72
128.38
127.39
127.35
126.80
125.46
122.22
119.63
118.77
108.84
103.19
40.39
40.12
30.14
Cl
O
N
f1 (ppm)

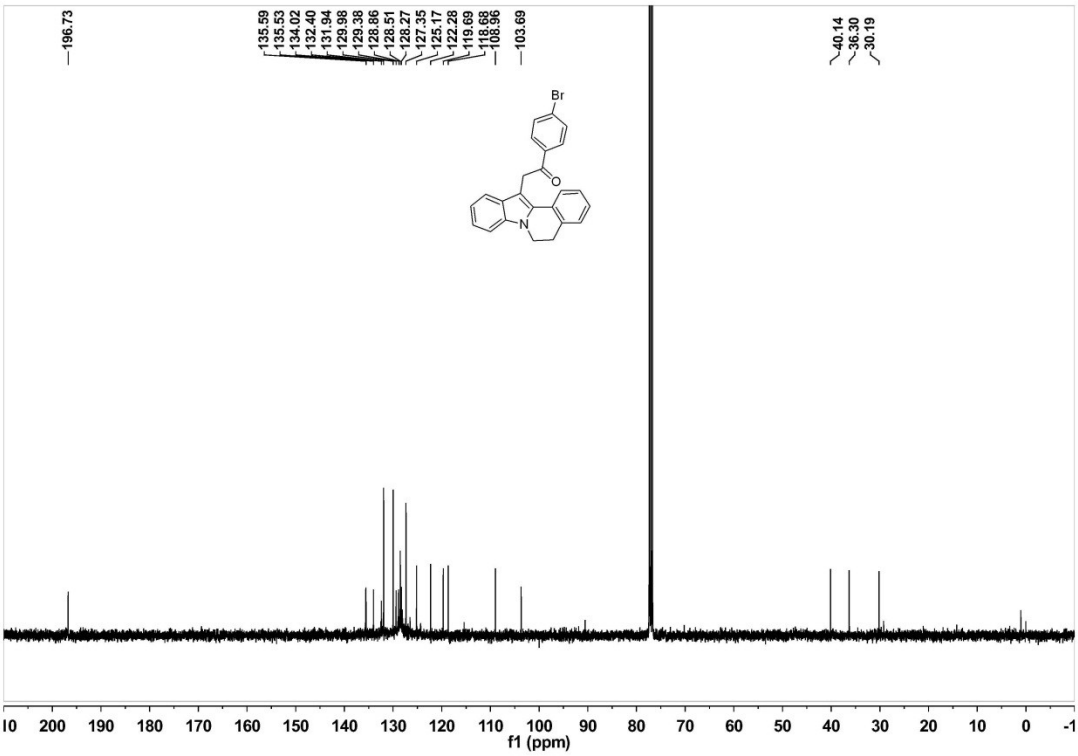
Compound 4c


8.188
7.999
7.980
7.684
7.664
7.579
7.561
7.484
7.464
7.339
7.333
7.320
7.313
7.299
7.257
7.253
7.247
7.236
7.217
7.197
7.103
7.085
7.065
4.719
4.260
4.245
4.229
3.129
3.113
3.098
Br
O
N
1.00
1.00
1.01
1.00
1.00
3.01
3.00
1.03
2.00
2.00
2.00
f1 (ppm)

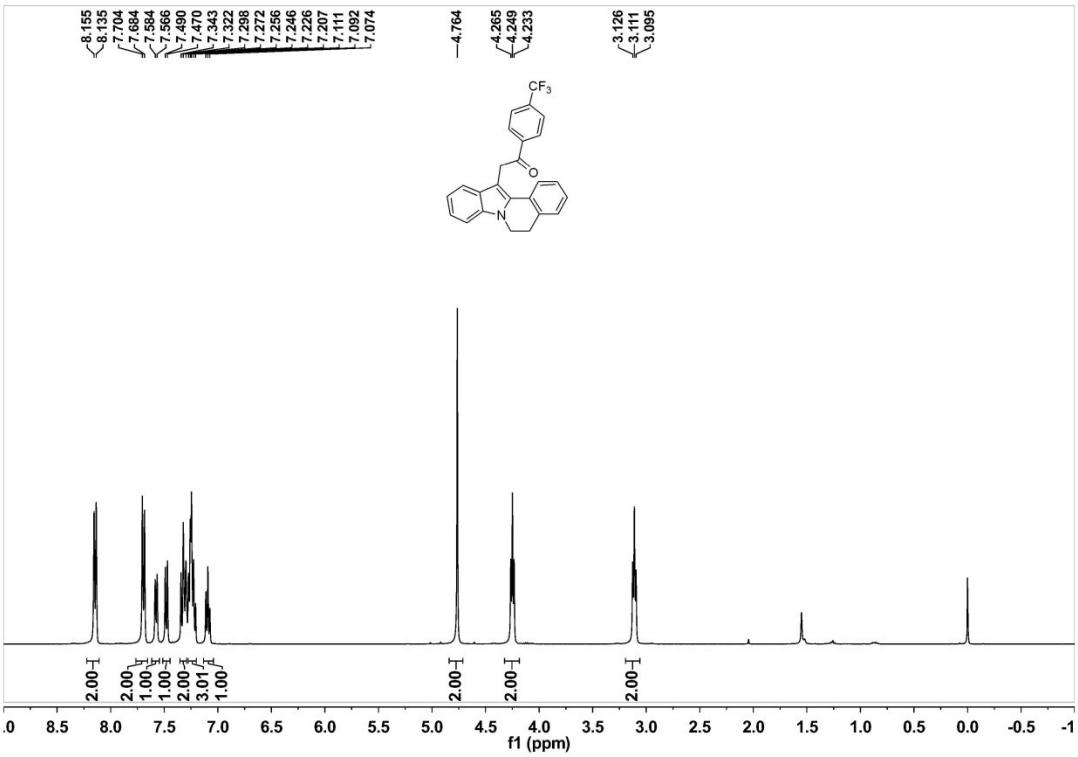

196.27
138.54
135.95
135.53
134.08
132.45
131.56
130.24
129.36
128.85
128.54
127.40
126.93
125.13
122.96
122.28
119.69
118.71
108.96
103.47
40.15
36.41
30.21
Br
O
N
f1 (ppm)

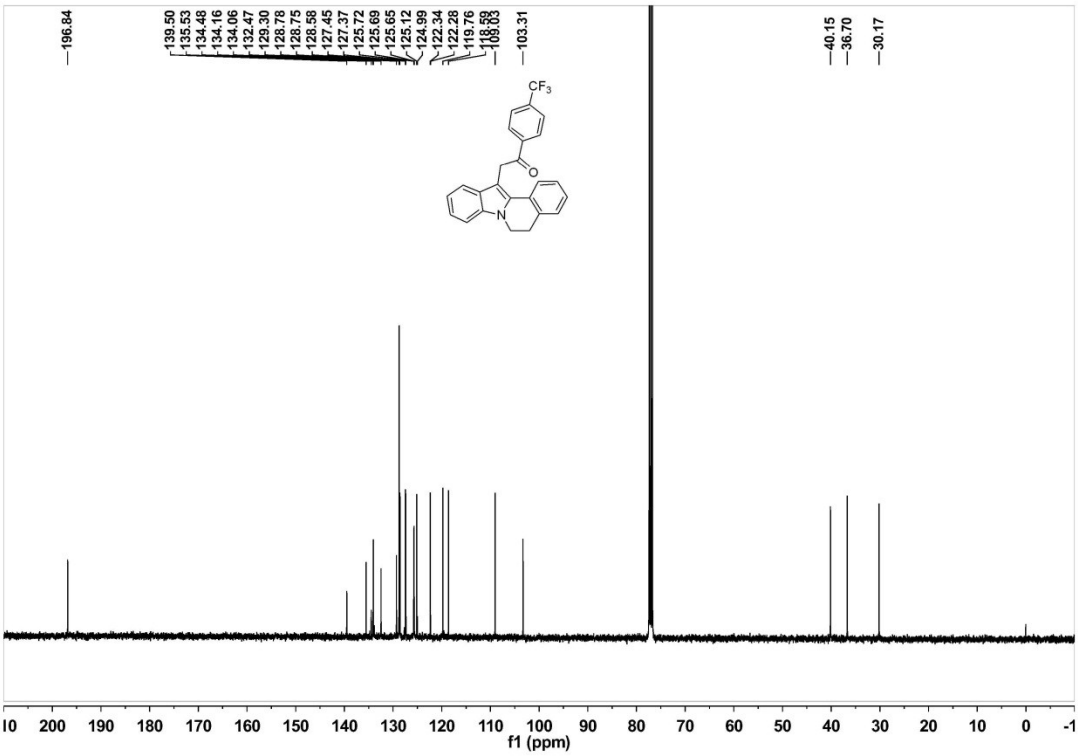
Compound 4d


7.946
7.925
7.599
7.594
7.587
7.577
7.487
7.467
7.343
7.322
7.299
7.240
7.222
7.204
7.105
7.085
7.067
4.719
4.278
4.262
4.246
3.143
3.127
3.112
Br
O
N
2.00
3.00
1.00
3.00
2.00
1.00
2.00
2.00
2.00
f1 (ppm)

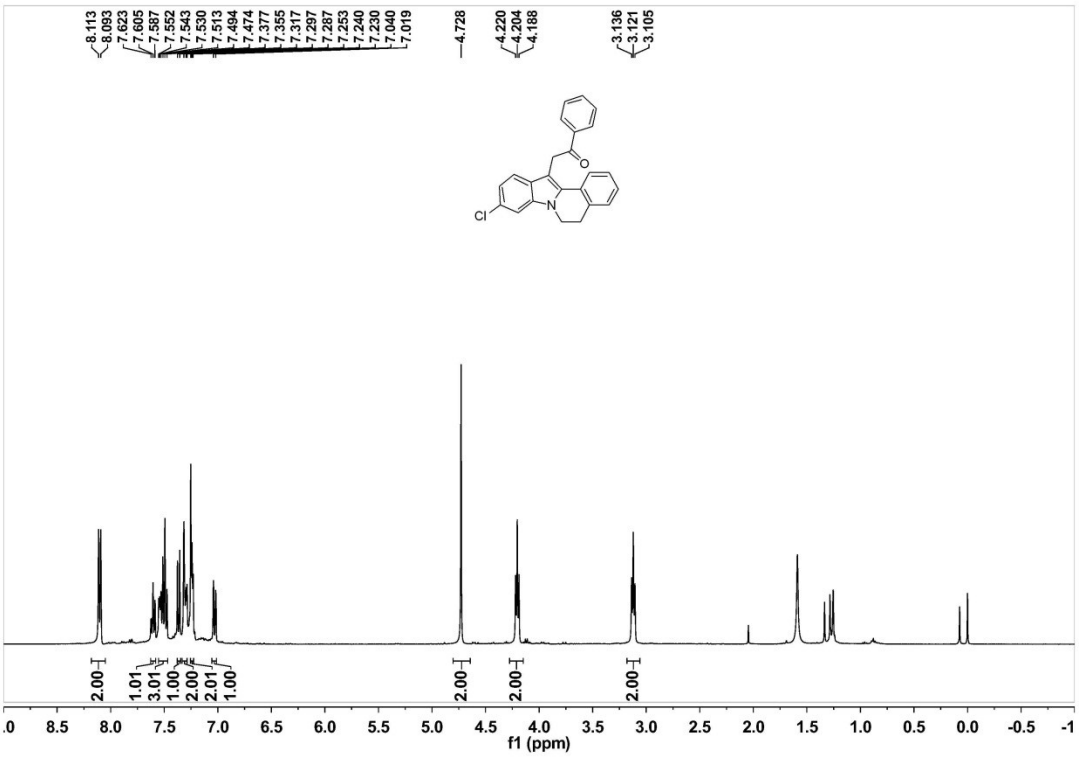

196.73
135.59
135.53
134.02
132.40
131.94
129.98
129.38
128.86
128.51
128.27
127.35
125.17
122.28
119.69
118.68
108.96
103.69
40.14
36.30
30.19
Br
O
N
f1 (ppm)

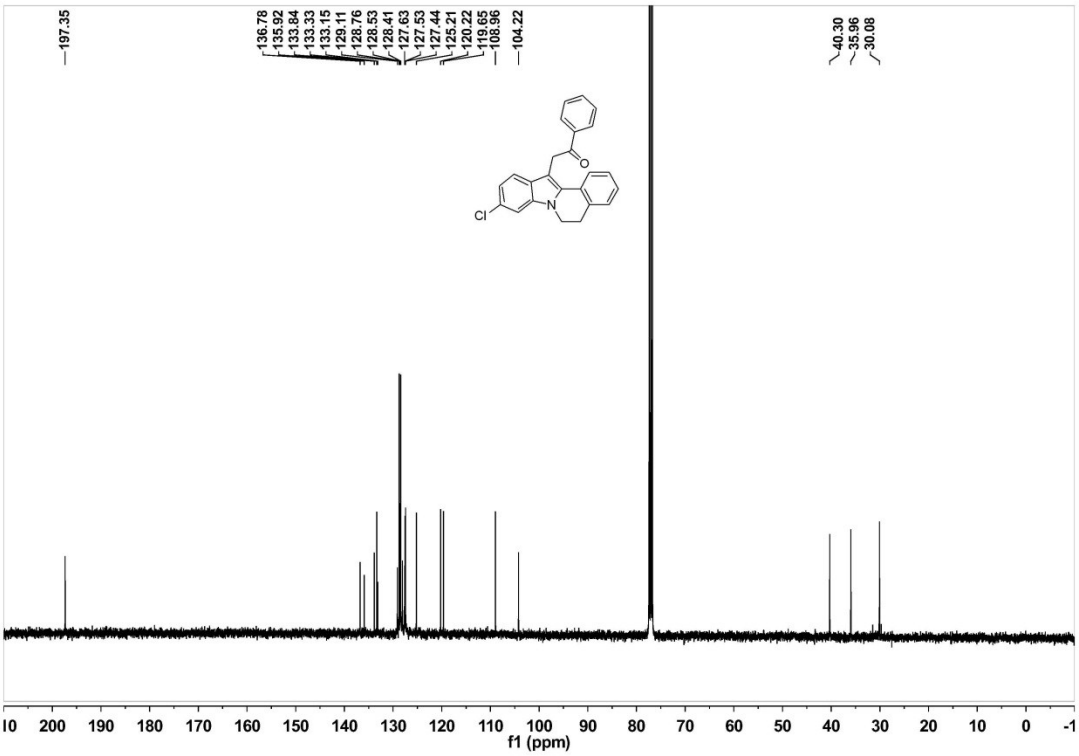
Compound 4e


8.155
8.135
7.704
7.684
7.584
7.566
7.490
7.470
7.343
7.322
7.298
7.272
7.256
7.246
7.226
7.207
7.111
7.092
7.074
4.764
4.265
4.249
4.233
3.126
3.111
3.095
CF3
O
N
2.00
2.00
1.00
1.00
2.00
3.01
1.00
2.00
2.00
2.00
f1 (ppm)

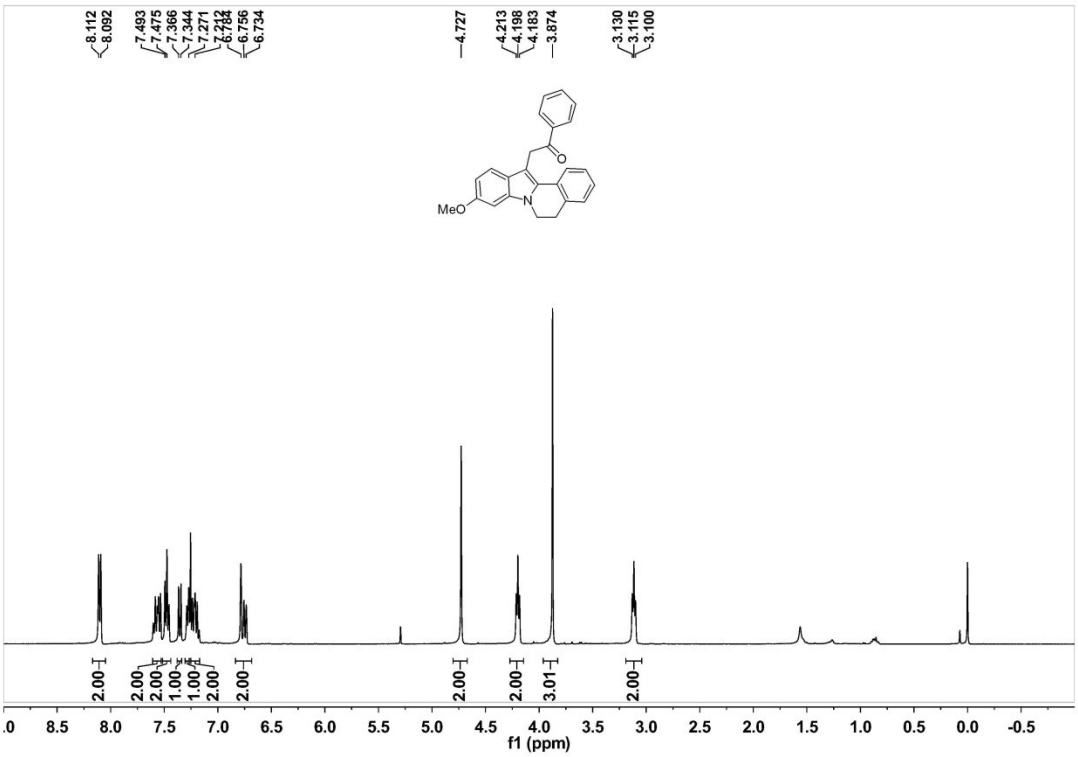

196.84
139.50
135.53
134.48
134.16
134.06
132.47
129.30
128.78
128.75
128.58
127.45
127.37
125.72
125.69
125.65
125.12
124.99
122.34
122.28
119.76
118.58
118.03
103.31
40.15
36.70
30.17
CF3
O
N
f1 (ppm)

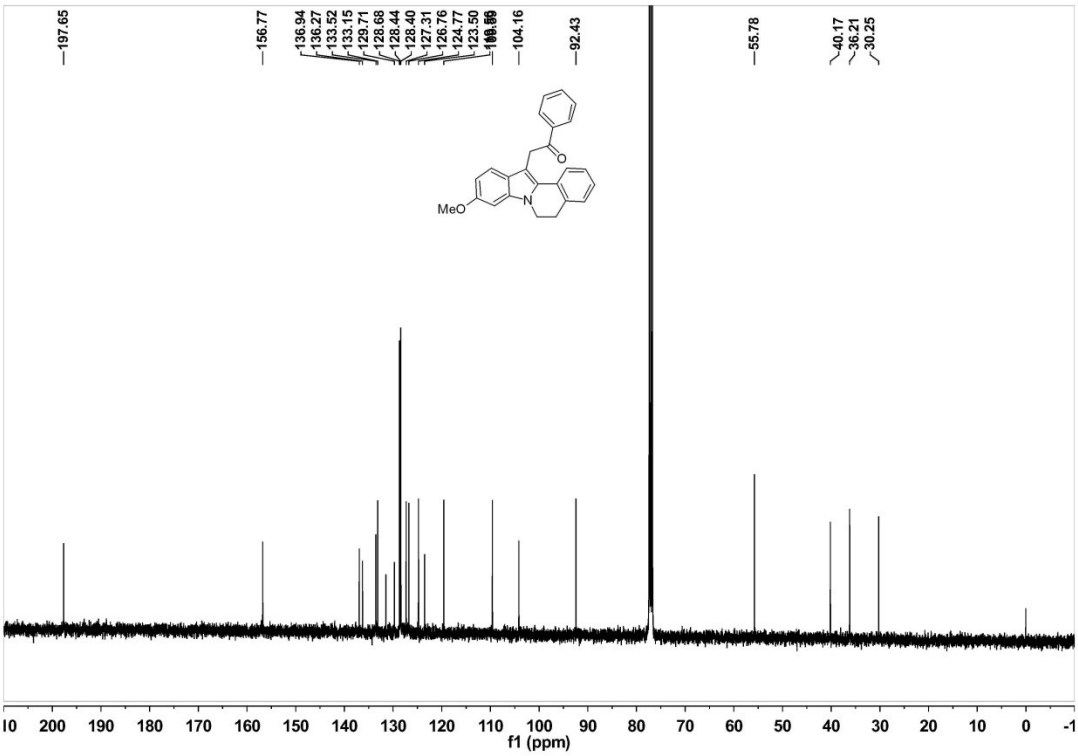
Compound 4f


8.113
8.093
7.623
7.605
7.587
7.552
7.543
7.530
7.513
7.494
7.474
7.377
7.355
7.317
7.297
7.287
7.253
7.240
7.230
7.040
7.019
4.728
4.220
4.204
4.188
3.136
3.121
3.105
Cl
O
N
2.00
1.01
3.01
1.00
2.00
2.01
1.00
2.00
2.00
2.00
f1 (ppm)

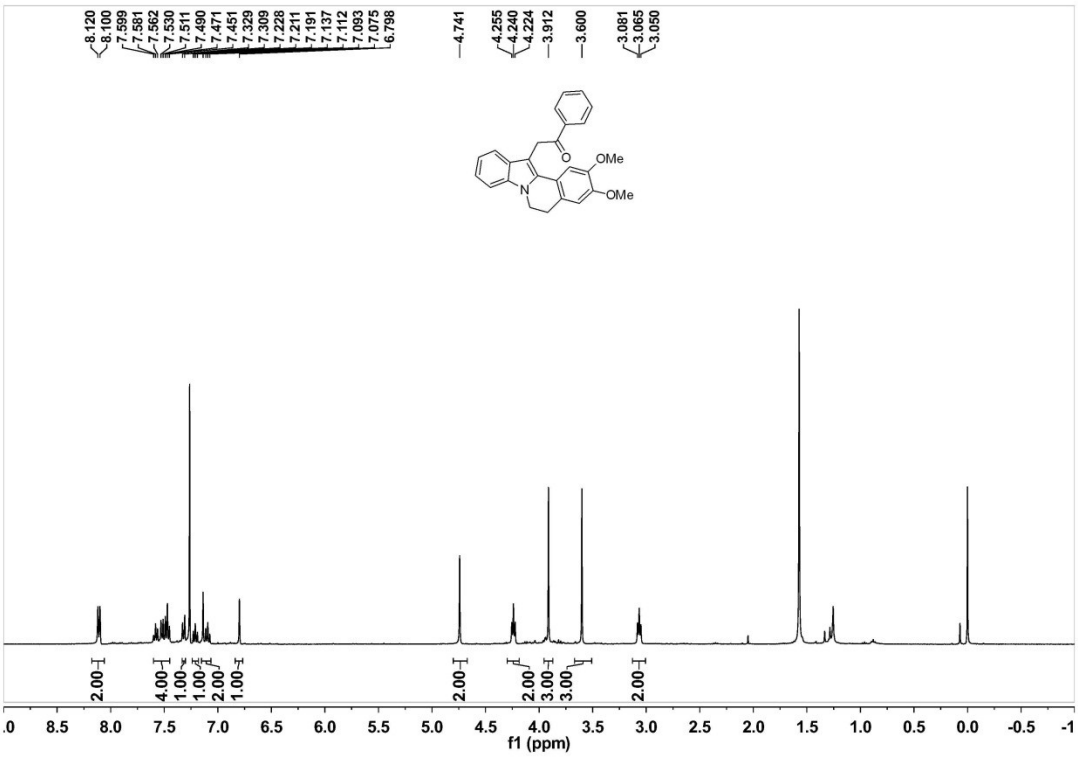

197.35
136.78
135.92
133.84
133.33
133.15
129.11
128.76
128.53
128.41
127.63
127.53
127.44
125.21
120.22
119.65
108.96
104.22
40.30
35.96
30.08
Cl
O
N
f1 (ppm)

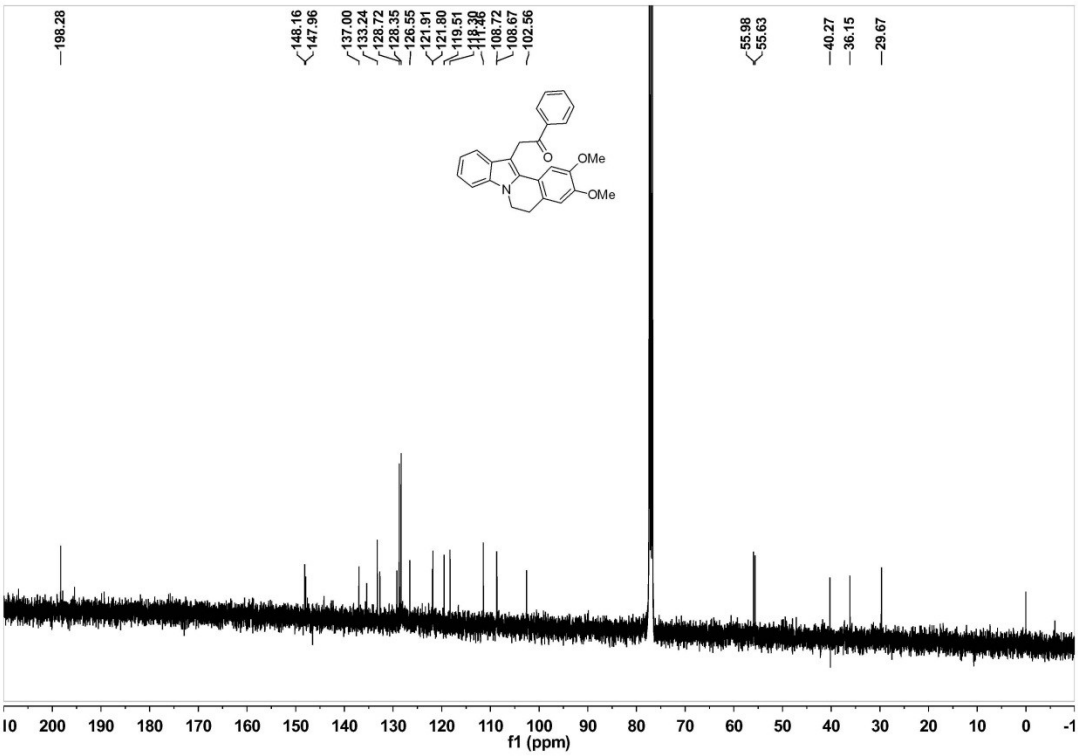
Compound 4g


8.112
8.092
7.493
7.475
7.366
7.344
7.271
7.212
6.784
6.756
6.734
4.727
4.213
4.198
4.183
3.874
3.130
3.115
3.100
MeO
2.00
2.00
2.00
1.00
1.00
2.00
2.00
2.00
2.00
3.01
2.00
f1 (ppm)

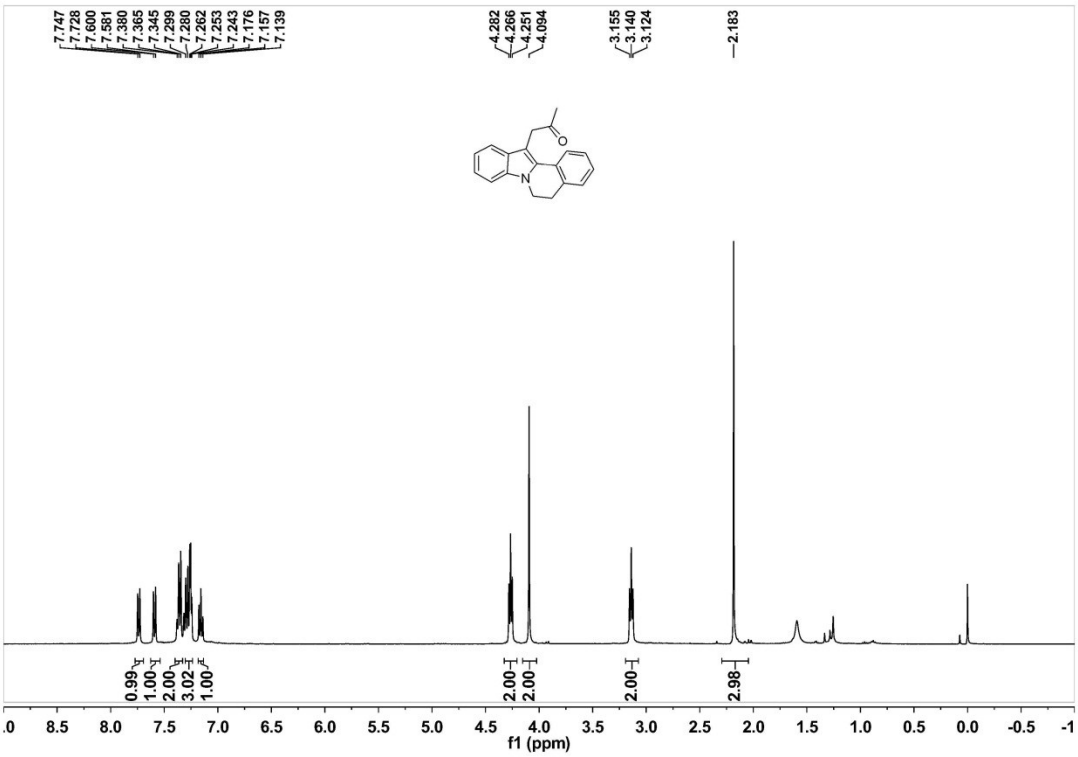

197.65
156.77
136.94
136.27
133.52
133.15
129.71
128.68
128.44
128.40
127.31
126.76
124.77
123.50
104.16
92.43
55.78
40.17
36.21
30.25
MeO
f1 (ppm)

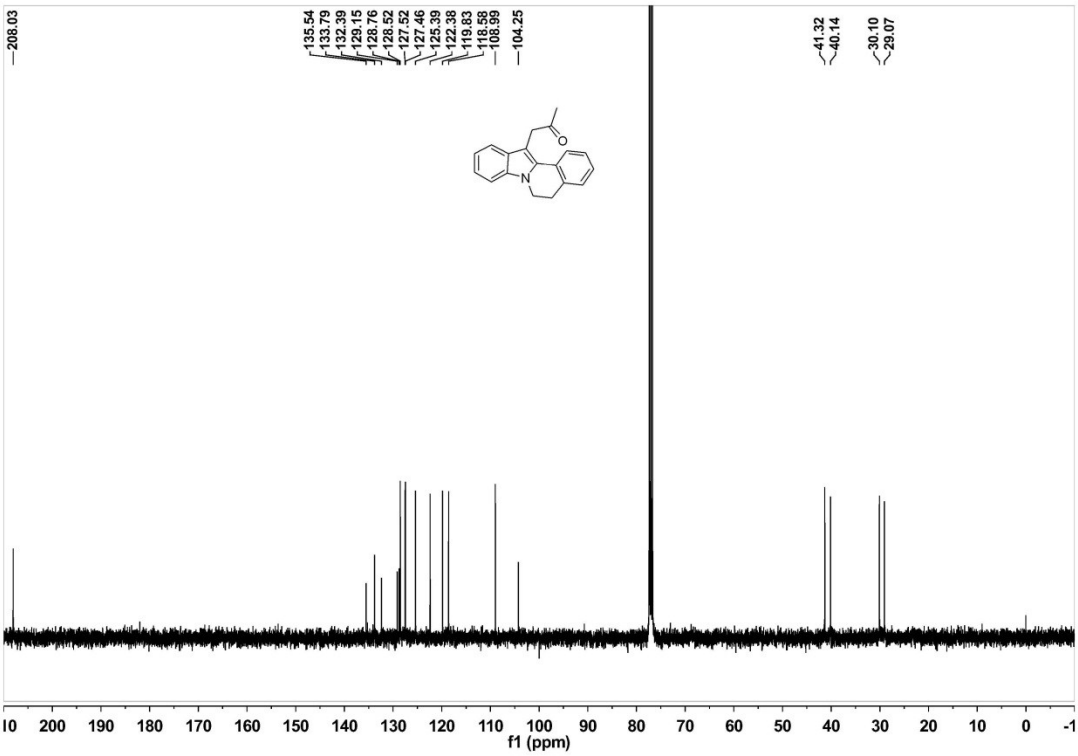
Compound 4h


8.120
8.100
7.599
7.581
7.562
7.530
7.511
7.490
7.471
7.451
7.329
7.309
7.228
7.211
7.191
7.137
7.112
7.093
7.075
6.798
4.741
4.255
4.240
4.224
3.912
3.600
3.081
3.065
3.050
OMe
OMe
O
N
2.00
4.00
1.00
1.00
2.00
1.00
2.00
2.00
3.00
3.00
2.00
f1 (ppm)

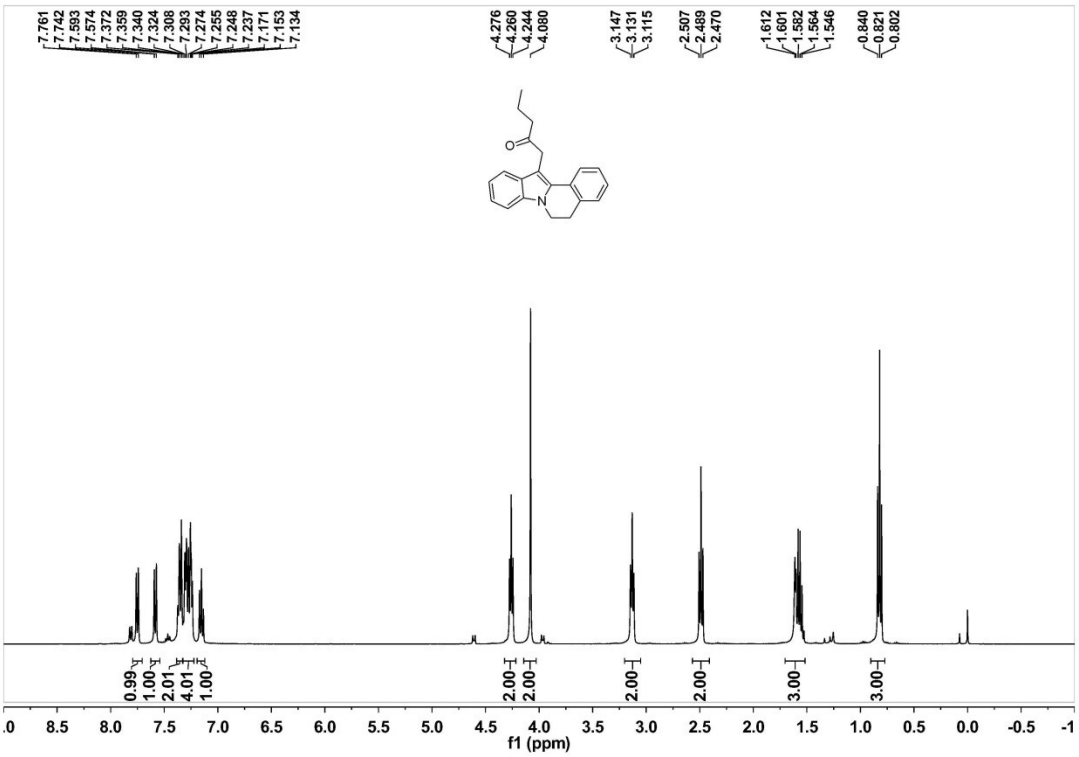

198.28
148.16
147.96
137.00
133.24
128.72
128.35
126.55
121.91
121.80
119.51
108.72
108.67
102.56
55.98
55.63
40.27
36.15
29.67
OMe
OMe
O
N
f1 (ppm)

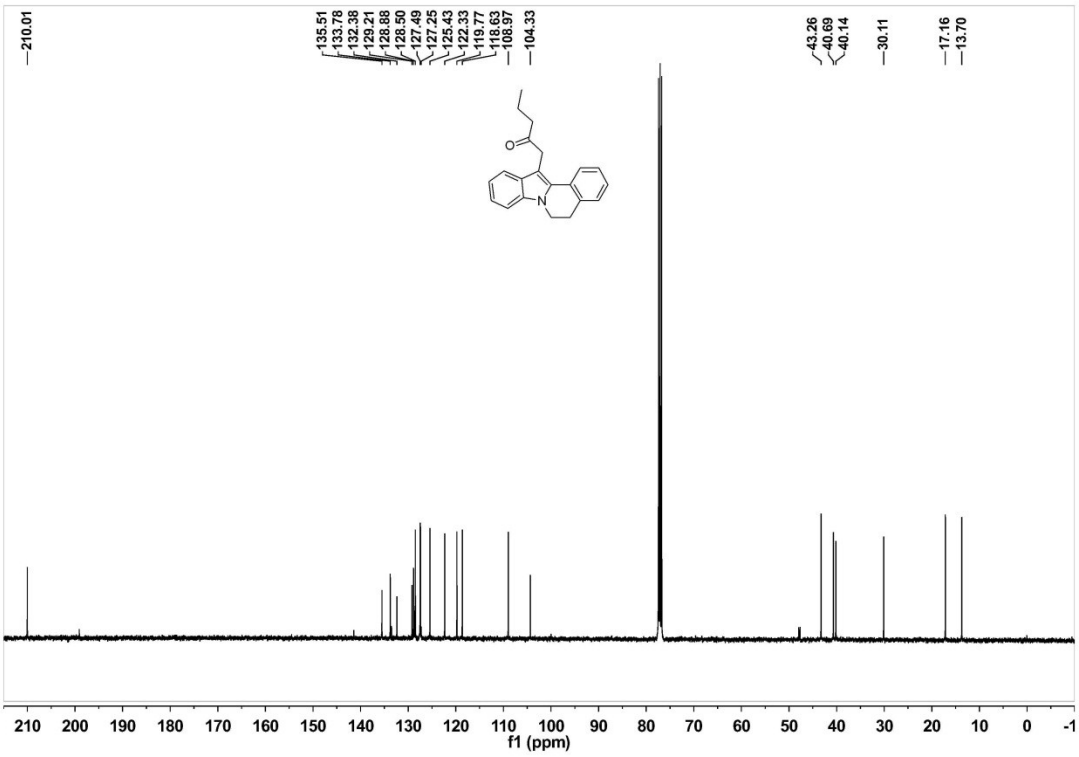
Compound 4i


7.747
7.728
7.600
7.581
7.380
7.365
7.345
7.299
7.280
7.262
7.253
7.243
7.176
7.157
7.139
4.282
4.266
4.251
4.094
3.155
3.140
3.124
2.183
0.99
1.00
2.00
3.02
1.00
2.00
2.00
2.00
2.98
f1 (ppm)

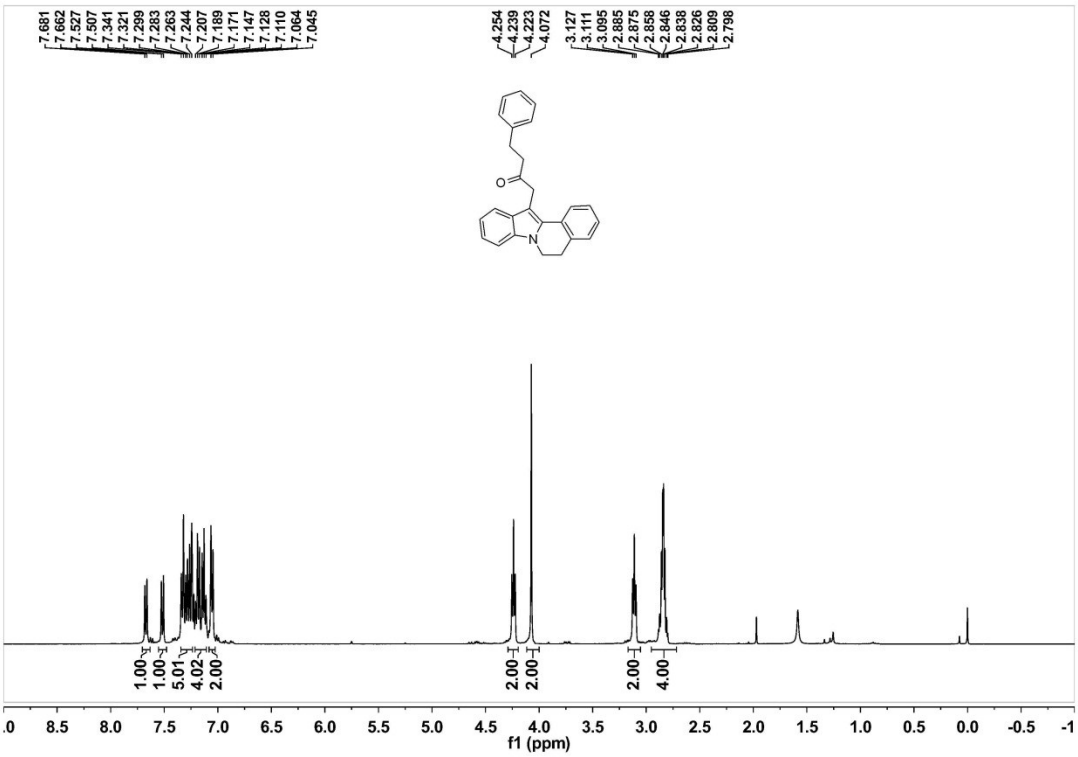

208.03
135.54
133.79
132.39
129.15
128.76
128.52
127.52
127.46
125.39
122.38
119.83
118.58
108.99
104.25
41.32
40.14
30.10
29.07
f1 (ppm)

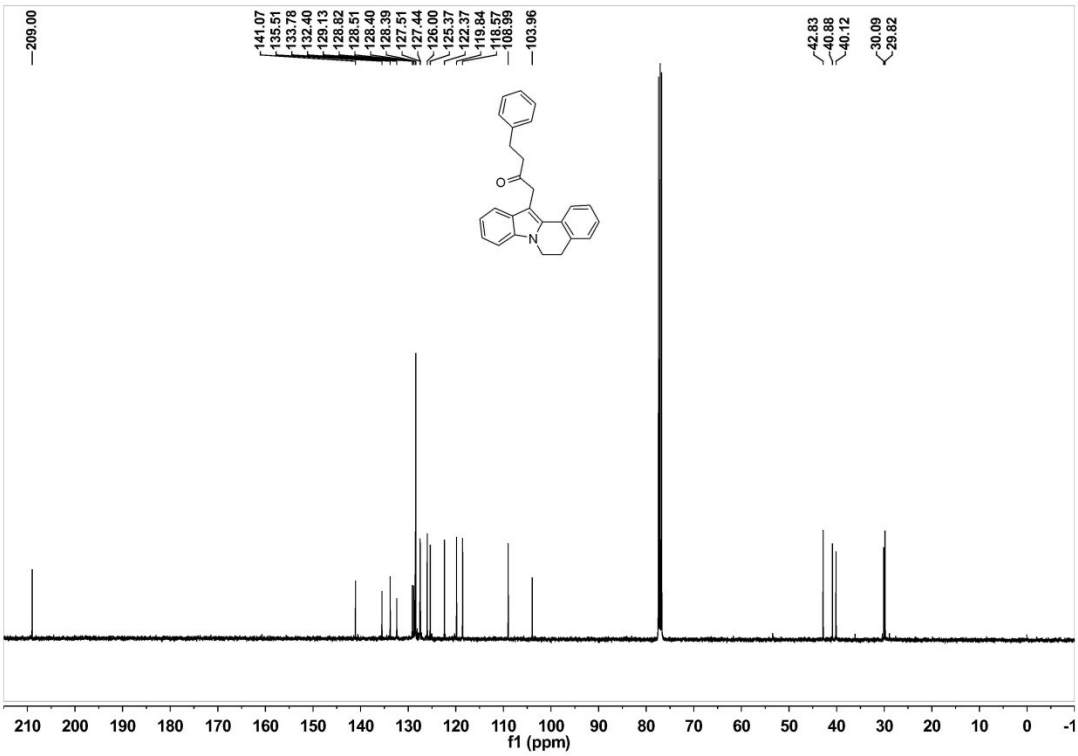
Compound 4j


7.761
7.742
7.593
7.574
7.372
7.359
7.340
7.324
7.308
7.293
7.274
7.255
7.248
7.237
7.171
7.153
7.134
4.276
4.260
4.244
4.080
3.147
3.131
3.115
2.507
2.489
2.470
1.612
1.601
1.582
1.564
1.546
0.840
0.821
0.802
0.99
1.00
2.01
4.01
1.00
2.00
2.00
2.00
2.00
3.00
3.00
f1 (ppm)

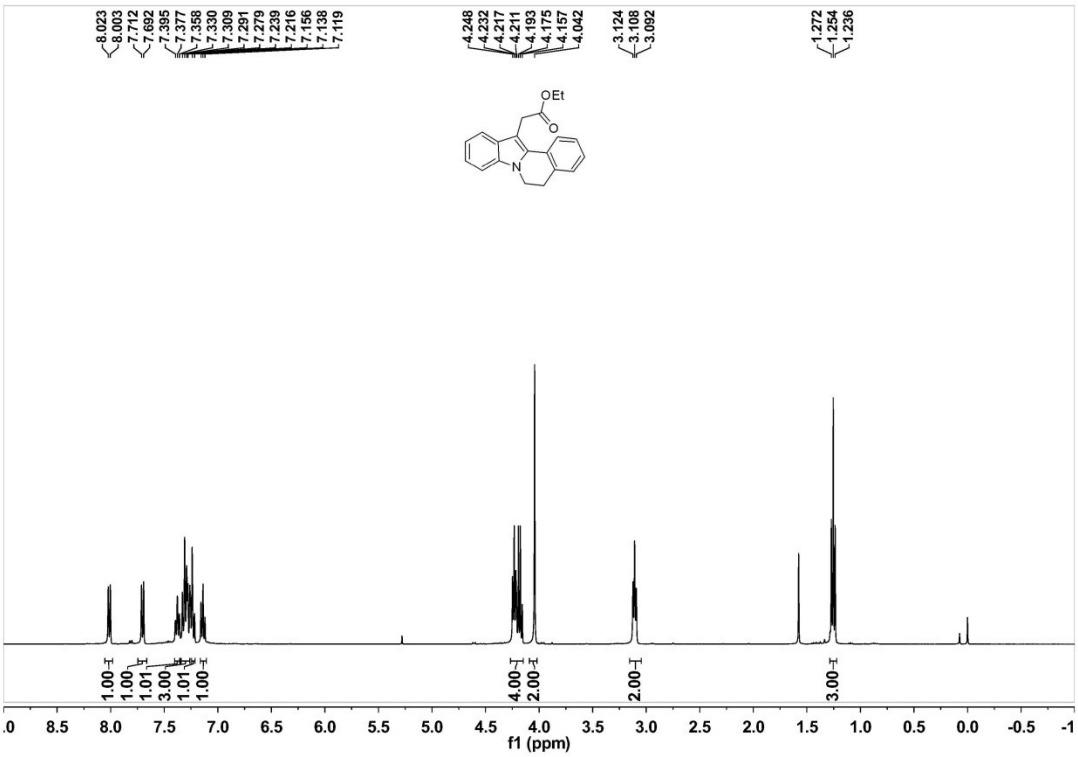

210.01
135.51
133.78
132.38
129.21
128.88
128.50
127.49
127.25
125.43
122.33
119.77
118.63
108.97
104.33
43.26
40.69
40.14
30.11
17.16
13.70
f1 (ppm)

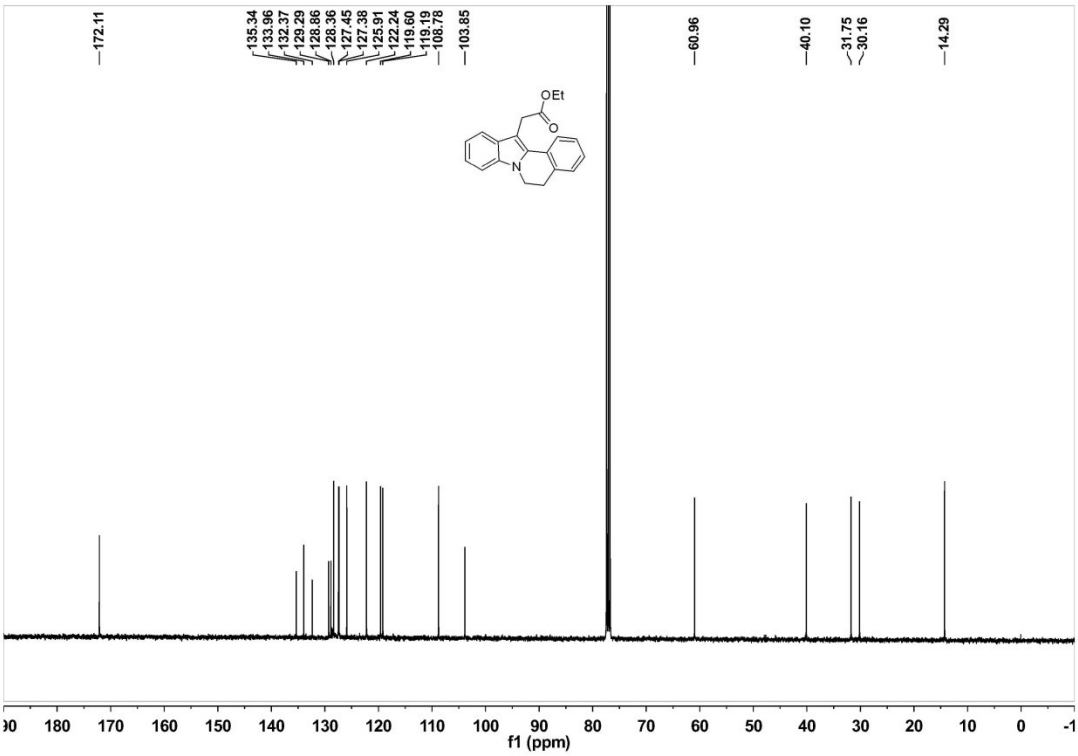
Compound 4k


7.681
7.662
7.527
7.507
7.341
7.321
7.299
7.283
7.263
7.244
7.207
7.189
7.171
7.147
7.128
7.110
7.064
7.045
4.254
4.239
4.223
4.072
3.127
3.111
3.095
2.885
2.875
2.858
2.846
2.838
2.826
2.809
2.798
O
N
1.00
1.00
5.01
4.02
2.00
2.00
2.00
2.00
4.00
f1 (ppm)


209.00
141.07
135.51
133.78
132.40
129.13
128.82
128.51
128.40
128.39
127.51
127.44
126.00
125.37
122.37
119.84
118.57
108.99
103.96
42.83
40.88
40.12
30.09
29.82
O
N
f1 (ppm)

Compound 4l


8.023
8.003
7.712
7.692
7.395
7.377
7.358
7.330
7.309
7.291
7.279
7.239
7.216
7.156
7.138
7.119
4.248
4.232
4.217
4.211
4.193
4.175
4.157
4.042
3.124
3.108
3.092
1.272
1.254
1.236
OEt
O
N
1.00
1.00
1.01
3.00
1.01
1.00
4.00
2.00
2.00
3.00
f1 (ppm)


172.11
135.34
133.96
132.37
129.29
128.86
128.36
127.45
127.38
125.91
122.24
119.60
119.19
108.78
103.85
60.96
40.10
31.75
30.16
14.29
OEt
O
N
f1 (ppm)